STUDIES IN THE CONCENTRATIONS AND CHEMISTRY OF CADMIUM IN THE ENVIRONMENT

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TABLE OF CONTENTS

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

Table of Contents continued...

LIST OF TABLES

List of Tables continued...

List of Tables continued...

List of Tables continued...

List of Tables continued...

List of Tables continued...

List of Tables continued...

LIST OF FIGURES

List of Figures continued...

List of Figures continued...

ABSTRACT

Seven surveys were conducted in the city of Christchurch (New Zealand) in order both to obtain comprehensive data describing the concentrations of cadmium in the environment, and determine factors likely to influence these concentrations. In three of the surveys—examining cadmium concentrations in air, riverwater and horse-chestnut leaves—samples were collected over long time periods. Levels of cadmium in dust and soil, house-dust, commercial products and foods were examined in the other four surveys. Concentrations of copper, lead and zinc were also measured in many cases.

Cadmium adsorption by—and mobility in—a Christchurch soil, weathering of a cadmium-containing paint and galvanized-iron, the behaviour of cadmium in samples being sequentially extracted, and speciations of cadmium in soils, road-dusts, house-dusts riverwater, and plastics were also studied.

High levels of cadmium were found in road-dust in the immediate vicinity of some industrial operations, but concentrations in the wider Christchurch environment were generally low. House-dusts contained higher concentrations of cadmium than typical external dusts. Cadmium concentrations in some commercial products were very high; however, there appeared to be little risk of cadmium being significantly mobilized during the use of most of these products. Probable daily intakes of cadmium were estimated. Numerous factors influenced the levels of cadmium in the various materials examined.

A Christchurch soil strongly adsorbed cadmium and the mobility of cadmium in this soil was low. Reagent selectivity for the forms of cadmium during sequential extraction was in some cases good and in some cases poor; little redistribution of cadmium occurred between phases during sequential extractions. Various factors were found to effect the adsorption and mobility of cadmium in soil, the outcome of each sequential extraction, and the weathering of cadmium from cadmium-containing paint and galvanized-iron.

CHAPTER 1
INTRODUCTION

1·1 Discovery, description and properties of cadmium

Cadmium was discovered in 1817 by Strohmeyer of Germany, who isolated it from calamine (zinc carbonate). The name cadmium is derived from *cadmia*, the ancient Greek name for calamine (Nriagu, 1980a, p36).

At atomic number 48, cadmium is positioned between zinc and mercury in Group IIB of the Periodic Table. Its electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$. The eight natural isotopes of cadmium yield a mean atomic weight of 112.40 (Förstner, 1980; Aylward and Findlay, 1974).

Elemental cadmium is a lustrous, silvery-white metal with a bluish tinge. It is soft, malleable and easily worked. Its crystal structure is distorted hexagonal-close packed. With melting and boiling points of 320.9 and 767.0 °C, respectively, cadmium is considered to be a relatively volatile metal. Cadmium vapour reacts rapidly in air to form brown cadmium oxide (CdO). The halogens, phosphorus, selenium, sulphur and tellurium also react readily with cadmium upon heating (Cotton and Wilkinson, 1976; Förstner, 1980; Schulte-Schrepping and Piscator, 1985).

Cadmium dissolves in most inorganic acids but, in contrast to zinc, is insoluble in alkaline media. Its standard reduction potential is –0.402 V at 25 °C. Cadmium halides, nitrate and sulphate are soluble whereas cadmium oxide, hydroxide, carbonate and sulphide are not (Förstner, 1980; Nriagu,1980a; Schulte-Schrepping and Piscator, 1985).

Cadmium and its salts are non-essential and toxic to humans, animals and plants (Förstner, 1980; Venugopal and Luckey, 1978; Kabata-Pendias and Pendias, 1985).

1·2 Anthropogenic utilization of cadmium

1·2·1 Occurrence, recovery and uses

Six cadmium minerals have been discovered: greenockite and hawleyite (the hexagonal and cubic forms of cadmium sulphide); otavite (cadmium carbonate); monteponite (cadmium oxide); cadmoselite (hexagonal cadmium selenide); and saukovite (cubic cadmium metacinnabar) (Bewers *et al.* 1987; Fleisher *et al.* 1974). None of these deposits are of sufficient size to warrant commercial extraction of cadmium (Schulte-Schrepping and Piscator, 1985).

Geochemically, cadmium is associated with minerals of zinc, lead and copper. Almost all cadmium produced is recovered as a by-product during the smelting of zinc ores, in which it is a minor (about 0.2%) isomorphic component (Förstner, 1980; Schulte-Schrepping and Piscator, 1985). Small additional amounts of cadmium are recovered during the processing of zinc-lead, zinc-copper and complex ores (Nriagu, 1980a, p48).

Cadmium and its compounds are used extensively in industry. A summary of these uses is given in Table 1·1.

Table 1·1

Uses and reasons for the use of cadmium in industry.[a]

Use	Cadmium products used[b]	Reasons for use	Examples of use
Cadmium coating and electroplating	Cd metal CdCN CdO $CdCl_2$ Cd complexes $CdSO_4$	Good corrosion protection (alkali and salt water), ductility, good frictional properties, high soldering potential, uniform and high rate of deposition, retention of luster	Coating nuts and bolts, automotive construction, aircraft parts, machine construction, defence industry
Nickel-cadmium, silver-cadmium & mercury-cadmium accumulator batteries	Cd metal $Cd(OH)_2$ $Cd(NO_3)_2 \cdot 4H_2O$	Long life, robust, cell reaction perfectly reversible, cell reaction doesn't release gas (can seal battery)	Power supply in portable appliances such as radios, calculators and pacemakers
Pigments (red, orange, yellow & maroon)	CdS CdSe CdO $CdCl_2$ $CdSO_4$ $Cd(NO_3)_2 \cdot 4H_2O$ Cd thioselenides Cd lithopones organocadmium salts	Bright deep shades, good covering power, high resistance to heat,light H_2S and SO_2	Colouring agent in ceramics, paper, plastics, printing inks, rubber, ruby glass, soaps and textiles
Plastics stabilizers	CdO $CdCl_2$ $CdSO_4$ organocadmium salts	Stabilize plastics to heat and light, work as antioxidants to retard discolouration	Production of PVC
Alloys-solders	Various Cd alloys *e.g.* "cerrobend" = 50%Bi; 26.7%Pb; 13.3%Sn; 10%Cd	Added Cd lowers the melting point of Ag, Cu and Zn	Joining dissimilar metals, soldering Al, hard soldering
Alloys-electrical	0.7%Cd; 99.3%Cu	Added Cd increases the strength of Cu wire without reducing conductivity	Overhead power lines to electric locomotives, automotive cooling fins, heavy-duty radiators
	2.5-15%Cd; 97.5-85%Ag	Added Cd reduces sparking	Electrical switches
Alloys-other	Various Cd alloys	miscellaneous properties	Nuclear control rods, fusible alloys in fire-protection devices, white-light lasers, lens grinding blocks
Other electrical uses	CdS CdSe CdTe CdO CdSb	Work as semiconductors, thermoelectric and photoelectric generators	Various electronics applications; thermodetectors, photovoltaic (solar) cells

Table 1·1 continued...

Use	Cadmium products used[b]	Reasons for use	Examples of use
	Cd arsenides Cd phosphides Cd borates CdF_2	Exhibit laser action, fluoresce	Laser beams, phosphors in television tubes, fluorescent lamps, X-ray screens
Catalysts	CdO Cd halides Cd dialkyls	Diverse catalytic properties	Organic polymerization reactions
Photography	$Cd(NO_3)_2 \cdot 4H_2O$ Cd halides	Various properties	Light-sensitive components of photographic film, flash powder
Pyrotechnics	Cd halides	Flammability and flame colour	Blue colour in fireworks
Fungicides		Toxicity	

Notes: **a.** Compiled from the following sources: Förstner, 1980; Hollander and Parker, 1978; Moore and Ramamoorthy, 1984; Nriagu, 1980a; Plunkert, 1988; Schulte-Schrepping and Piscator, 1985.
b. May be used directly, used as a starting material, or be only occasionally used.

1·2·2 Consumption patterns

Nine-tenths of the cadmium utilized by industry in 1986 was in the first four usage categories listed in Table 1·1: coating and plating, battery production, pigments and stabilizers (Plunkert, 1988). In Table 1·2 a list of the percentage consumption figures for each of these categories for selected years is presented for the period 1974–1986.

Table 1·2

Percentage consumption of cadmium by usage category during the period 1974–1986.

Usage	1974[a]	1980[b]	1981[c]	1984[d]	1986[e]
Coating and plating	35	34	34	34	32
Battery production	15	16	16	27	29
Pigments	25	27	27	16	16
Plastics stabilizers	15	15	15	15	15
Alloys and other uses	10	8	8	8	8

Notes: **a.** Nriagu, 1980a **b.**Reese, 1982 **c.**Plunkert, 1983 **d.**Plunkert, 1986 **e.**Plunkert, 1988

Total world production of cadmium over the same period (1974–1986) remained more or less constant at a mean value of 17 710 (metric) tons yr^{-1} (standard deviation 1 034 tons yr^{-1}) (calculated from figures of Nriagu, 1980a, p52; Reese, 1982; Plunkert, 1988). Given this fact, the data in Table 1·2 indicate that over the 12 years shown, a decreasing

tendency to use cadmium-based pigments was offset by an increasing demand for cadmium in battery production.

Until 1871, when the first commercial uses for cadmium were found, yearly production of the metal remained below 100 kg (Nriagu, 1980a, p49). From then until 1969, production and consumption increased steadily. Yearly production first exceeded 100 tons in 1916, 1000 tons in 1928 and 10 000 tons in 1960. Since 1960, when 17 573 tons of cadmium were recovered, production has remained relatively static. The mean amount of the metal produced yearly during the period 1969–1986 was 17 426 tons (standard deviation 1 064 tons). In 1986, 18 257 tons of cadmium were produced (Plunkert, 1988; Reese, 1982; Nriagu, 1980a, p53).

1·3 Concentrations, sources and chemistry of cadmium in the environment

1·3·1 Concentrations and sources

Contamination of the environment by cadmium is brought about both by natural and man-made means. Natural production and cycling of cadmium gives rise to an ubiquitous background level of the element; a level which varies depending on local geographic features. For example, sedimentary rocks (and soils derived from them) tend to have higher concentrations of cadmium than other rock and soil types (Bewers *et al.* 1987; Gong *et al.* 1977).

The mean concentration of cadmium in the earth's crust is estimated to be 0.11 $\mu g\ g^{-1}$ (Förstner, 1980). Other background estimates for the metal are: air, 0.01–1.0 $ng\ m^{-3}$ (Bewers *et al.* 1987; Nriagu, 1980a); freshwater, 0.010–0.07 $\mu g\ l^{-1}$ (Ahlers and Hunter, 1988; Förstner, 1980); seawater, 0.001–0.075 $\mu g\ l^{-1}$ (Florence, 1982; Hunter, 1982; Hunter and Ho, 1984); rainwater, 0.1–1 $ng\ l^{-1}$ (Bewers *et al.* 1987); and Antarctic ice, about 0.1–0.2 $pg\ g^{-1}$ (Batifol *et al.* 1989; Dick, 1988).

It is onto this natural background level that any cadmium produced by anthropogenic means is added. Cadmium liberated to the atmosphere serves to illustrate this effect. Natural sources of cadmium to the atmosphere include forest fires, volcanoes, sea-salt spray, wind-borne soil particles, the sloughing of vegetation and possibly the degassing of crustal rocks (Nriagu,1989; Nriagu, 1980a). The predominant anthropogenic sources are non-ferrous metal production, waste incineration and fertilizer manufacture (Nriagu and Pacyna, 1988; Nriagu, 1980b). Nriagu estimated that in 1983, global cadmium emissions to the atmosphere from anthropogenic sources (76 tons) exceeded those from natural sources (13 tons) by a factor of five (Nriagu, 1989).

After about one week, 70% of the cadmium released to the atmosphere during a given day is redeposited on the land (the other 30% falls on the oceans) (Nriagu, 1980b). Since cadmium settles on the land at a faster rate than natural or anthropogenic processes remove it, a net accumulation of the metal occurs. Analysis of an archived soil collection in Britain revealed that the soil burden of cadmium attributable to atmospheric deposition alone had increased by between 27 and 55% since the year 1850 (Jones and Symon, 1987).

Farmlands may gain more cadmium than other land areas due to the repeated application of phosphatic fertilizers or sewage sludges, both of which can contain appreciable quantities of the element (Rothbaum *et al.* 1986; Brown *et al.* 1983; Jones and Symon, 1987; Förstner, 1981). This has caused a fair degree of concern, the reason being that of all the common heavy metals it is cadmium which shows the greatest tendency to accumulate in food plants, and so enter the food chain (Sherlock and Smart, 1986; Kabata and Pendias, 1985). Further aspects of this subject are dealt with in Chapters 2, 6, 10 and 11.

Cities usually contain a wide range of cadmium sources. Examples include car tyre wear, combustion, water runoff from galvanized products and various industrial operations—some cadmium based and some not (Ward *et al.* 1977; Hollander and Parker, 1978: Förstner, 1980; Nriagu, 1980a). Sources of cadmium in the urban environment are examined further in Chapters 2–5, 7–9 and 13.

1·3·2 Environmental chemistry

The chemistry of cadmium, and interactions between cadmium and its immediate environment, determine its toxicity and mobility patterns. The prime mobile species of cadmium in soils is the divalent ion, Cd^{2+}, the formation of which is favoured at positive values of the redox potential and pH values of less than 8 (Hermann and Neumann-Mahlkau, 1985). The presence of certain types of organic compounds in the soil may increase or decrease cadmium's mobility, due to the formation of organocadmium bonds, and other interactions between cadmium and organic ligands (Ram and Verloo, 1985). These interactions and other physical factors (such as rainfall and the soil's density, porosity and sorption characteristics) determine the amount of cadmium taken up in crops, the fraction retained by the soil and the amount which leaches from the soil to the water table (Amacher *et al.* 1988; Baes and Sharp, 1983; Christensen, 1985). Similarly, the toxicity of cadmium to humans is a direct result of the chemical interactions which occur once it has entered the human body. Thus, the availability and toxicity of cadmium to human populations is dependent on its speciations, the nature and properties of its immediate environment and the interactions between them.

An overview of the human toxicology of cadmium comprises the next section of this introduction. Further discussions of aspects of cadmium's chemistry are found in Chapters 10–13 (in particular) and within the "results and discussion" sections of most other chapters.

1·4 The human toxicity and toxicology of cadmium

1·4·1 Historical overview

Although cadmium was not identified as an element until 1817, a possible reference to its harmful effects appeared in the writings of Agricola, a sixteenth-century miner (Nriagu, 1980a). What are now considered to be the first medically documented cases of cadmium poisoning happened in 1858. Three servants developed acute respiratory and

gastrointestinal problems a short time after polishing silverware with cadmium carbonate dust (Berman, 1980). However, it was not until 1920 that cadmium poisoning as such was definitively recognized (Yasumura *et al.* 1980).

During World War I, due to an excessive demand for tinned food and the resulting tin shortage, cadmium was used in food containers as a substitute for tin. By the early 1920's several cases of acute cadmium poisoning had occurred (which were reported in the literature) in people who had ingested acidic foods stored in cadmium-lined containers (Schroeder, 1974). The practice was temporarily given up. Cadmium was also utilized pharmaceutically in the mid-1920's for the treatment of malaria, syphilis and tuberculosis, but this usage was abandoned once the metal's toxicity became widely known (Waldbott, 1973; Berman, 1980).

Despite this knowledge, numerous new cases of acute cadmium poisoning (some fatal) were reported during the 1930's, which were traced to the use of cadmium-plated ice-cube trays, coffee-urns and cooking utensils (Berman, 1980).

A few years later during World War II, cadmium oxide fumes were assessed with regard to their potential as a chemical weapon (Yasumura, 1980). Surprisingly, at the same time, due to the loss of Malayan tin, cadmium was again investigated as a possible substitute for tin cans (Schroeder, 1974).

By 1945, the industrial uses of cadmium and its compounds were firmly established; 4 389 tons of the metal were produced worldwide in that year (Nriagu, 1980a). Unfortunately, concurrent with the emergence of cadmium-based industries came cases of occupational exposure to the element and its compounds (Friberg *et al.* 1974). These have taken the forms both of acute and chronic poisonings.

The most frequent cases of acute occupational cadmium poisoning have been among people involved in welding, soldering or cutting cadmium alloys and cadmium-plated metals (Schulte-Schrepping and Piscator, 1985). One of the characteristics of acute cadmium poisoning is that there is usually some delay before the onset of symptoms. Lethal doses of cadmium fumes have been inhaled without the workers feeling much discomfort (Berman, 1980). According to Yasumura *et al.* (1980) "In a large number of cases it is the naive, careless, or untrained worker who is at greatest risk of acute poisoning."

Chronic occupational cadmium poisoning, occurring by exposure to a relatively low concentration of the element or its compounds over a long time period (as distinct from acute intoxication) remained unrecognized until 1948. In that year Friberg identified the disease among workers in a Swedish alkaline battery factory, who had been exposed to cadmium oxide dust (Friberg *et al.* 1974, p95). Emphysema of the lungs and renal damage were observed in exposed workers. Subsequent studies worldwide confirmed Friberg's findings and identified other potentially hazardous cadmium related industries (Berman, 1980; Yasumura *et al.* 1980; Friberg *et al.* 1975, pp95–99).

As a result of the concern generated by the results of such studies, industrial cadmium abatement programs were introduced in many countries. However, occupational

cases of acute and chronic cadmium poisoning were still common in 1980 (Piotrowski and Coleman, 1980; Yasumura *et al.* 1980).

Although in recent times (post 1950) the frequency of acute cadmium poisoning cases has been far lower among the general population than it has among occupationally exposed groups, the seriousness of such incidents should not be underestimated. Berman (1980) cites the case of a two year old child who died as a result of chewing the cadmium-based paint from his cot.

The other possibility, *chronic* intoxication among a general population, occurred in 1948 (and was definitively diagnosed as such in 1961) among several hundred persons from villages on the banks of the Jintsu River, Toyanna Prefecture, Japan (Förstner, 1980; Friberg *et al.* 1974; Nogawa *et al.* 1989). Cadmium fumes and particulate matter emitted from a nearby lead and zinc mining company caused an excessive accumulation of the metal in the soil of the Fuchi-machi farming community (Waldbott, 1973). Rice and soybeans grown in this soil contained high concentrations of cadmium (mean value 1.0 $\mu g\ g^{-1}$, and up to 3.0 $\mu g\ g^{-1}$) (Piotrowski and Coleman, 1980). The most prominent symptom was that the bones fractured under slight pressure, due to their decalcification and subsequent softening. A large amount of pain was involved in this process, and the sickness became known as *itai-itai* disease, which is variously translated *it hurts-it hurts* or *ouch-ouch* disease (Berry *et al.* 1974). It has been estimated that by the end of 1965, nearly 100 deaths had resulted from the disease (Friberg *et al.* 1974). Most of the victims were multiparous women over 50 years of age. Due to the presence in each of the patients of other factors, such as a low calcium intake, it is now assumed that cadmium is a necessary but not sufficient factor for the development of itai-itai disease (Piotrowski and Coleman, 1980).

Itai-itai disease served to highlight the insidious nature of environmental cadmium poisoning. The fact that it was many (typically 30–40) years before the onset of symptoms suggested that an accumulation of cadmium sufficient in the long term to cause chronic intoxication was already taking place among other communities. Numerous environmental studies were undertaken in many countries, and a number of sites (mainly aquatic) were discovered to be heavily polluted with cadmium (Förstner, 1980).

Investigations have also been carried out in such areas as edible plant uptake and accumulation of cadmium (*e.g.* Elsokkary, 1980; Eriksson, 1988; Sharma, 1980; Symeonides and McRae, 1977); the mobility and sorption characteristics of cadmium in soils (*e.g.* Christensen, 1985; O'Connor *et al.* 1984; Trefry,1984; Navrot *et al.* 1978; Garcia-Miragaya and Page, 1977; Puls and Bohn, 1988); the amount of cadmium in aerosols (*e.g.* Khandekar *et al.* 1981; Noller and Bloom, 1980); the levels of cadmium in food and cigarettes (*e.g.* Spivey-Fox, 1988; Sherlock and Smart, 1986; Brooks and Trow, 1979); and the toxicology and metabolism of cadmium (*e.g.* Hutton, 1983; Venugopal and Luckey, 1978).

1·4·2 Absorption and accumulation of cadmium in humans

The two principal means by which cadmium is absorbed into the human body are inhalation and ingestion (breathing and eating) (Förstner, 1980). It has been estimated that between 25 and 50% of inhaled cadmium is absorbed by the lungs whereas only about 6% of ingested cadmium is absorbed by the gastrointestinal tract. Notwithstanding this, food accounts for about 90% of the individual body burden of cadmium in an "uncontaminated" population, as the levels of cadmium in food are normally far higher than those ordinarily prevalent in the atmosphere. Air and drinking water supply an estimated 4–7% and 2–4%, respectively, of the average daily intake (Yasumura *et al.* 1980; Förstner, 1980; Fleisher *et al.* 1974).

An exception exists in the case of smokers, due both to the ability of the tobacco plant to accumulate cadmium from the soil and to the fact that a large part of the inhaled dose is absorbed (Brooks and Trow, 1977). Kidneys of (previous) smokers generally contain twice as much cadmium as those of non-smokers; indicating that in smokers, the intake of cadmium from cigarettes can equal or exceed the intake from food (Schulte-Schrepping and Piscator, 1985).

No homeostatic mechanism has been located by which the amount of cadmium in the human body may be regulated (Venugopal and Luckey, 1978). For this reason, the amount of cadmium in a person increases with that person's age, from an estimated 1 μg at birth to between 15 and 80 mg in the 50 year old (not occupationally or environmentally exposed to a significant degree) depending on geographic locality and personal history (Förstner, 1980). The mean residence time of cadmium in humans has been calculated to lie somewhere between 20 and 40 years (Förstner, 1980; Nriagu, 1980b).

Of the cadmium absorbed by the body, 47% is sequestered in the liver and the cortex of the kidneys. Another 3% of the body burden is shared between the lungs and pancreas. The remaining 50% ends up more or less evenly distributed among the other tissues (Berry *et al.* 1974; Ivengar *et al.* 1978; Yasumura *et al.* 1980).

1·4·3 Effects and symptoms of cadmium intoxication in humans

Cadmium is regarded as a highly toxic metal. The lethal dose to humans has been estimated to be 0.35–9 g by ingestion and 1900 min mg m^{-3} (*e.g.* 190 mg m^{-3} for 10 min) by inhalation (Yasumura *et al.* 1980). Death occurs 24 hr to 2 wk later. Chronic effects may range from molecular disruption through to the death of the subject (Piotrowski and Coleman, 1980).

The effects and symptoms of cadmium poisoning are listed in Table 1·3

Table 1·3[a]

Effects and symptoms of cadmium poisoning.

Bodily part	Effects and symptoms	Comments
Kidney	Kidney damage; lesions on the proximal tubules, reduced ability to concentrate urine, cloudy urine, proteinurea (protein in the urine), glycosuria, amino-aciduria, hypercalcuria, presence of cadmium, albumin and excess phosphate in the urine, amyloid deposits in the kidney, kidney-stone formation	Observed in cases of acute and of chronic intoxication
Liver	Cirrhosis (distortion and scarring of the liver, with associated loss of function)	Chronic and acute cases
Lungs and related	Anosmia (impaired sense of smell due to damage to the olfactory nerve) persistent coughing and choking, dyspnea (shortness of breath). Usual outcome is pulmonary emphysema (loss of alveolar elasticity) with or without bronchitis and/or pneumonia	From inhaled cadmium, chronic and acute Cd was once used to treat tuberculosis (!) (section 1·4·1)
Heart and related	Hypertension (high blood pressure), chest cramps, thrombi in the coronary artery (heart blood clots)	Chronic and acute cases
Bones	Osteomalacia (bone demineralization) due to decreased gastrointestinal Ca absorption, osteoporosis (bone softening) with tendency to fracture, leg myalgia (muscle pain), waddling gait	Chronic poisoning only
Digestive system	Dryness of mouth and excessive salivation, sore throat, yellowing of the teeth, persistent vomiting, abdominal pains, diarrhoea, severe ulcerative gastroenteritis and congestion, poor appetite (leading to weight loss)	Acute oral poisoning
Other effects	Growth retardation, impaired reproductive function, possibly neoplasia (tumor formation) and teratogenic (mis-shapen organ formation) effects	Chronic effects

Note: **a.** Compiled from Berman, 1980; Berry and Osgood, 1974; Fleisher *et al.* 1974; Förstner, 1980; Purves, 1985; Schulte-Schrepping and Piscator, 1985; Tortora and Anagnostakos, 1984; Venugopal and Luckey, 1978; Waldbott, 1973; and Yasumura *et al.* 1980.

The most common effects of cadmium poisoning are kidney damage, cirrhosis of the liver and lung disease (Table 1·3). There is evidence to suggest that cadmium acts as a highly specific inducer of metallothionein, a small sulphydryl-rich and low molecular weight protein synthesized in the liver and kidneys. The resultant cadmium-thionein complex serves the purpose of temporarily inhibiting cadmium's toxic activity. Once the amount of metallothionein available is insufficient to complex all the cadmium, the toxicity of the metal is felt (Mason, 1984; Förstner, 1980). In other words, a threshold level of cadmium must be exceeded before serious renal or hepatic damage begins (probable kidney value: 200 $\mu g\ g^{-1}$) (Piotrowski and Coleman, 1980). Unfortunately, by the time that the symptoms of renal damage manifest, the kidneys have already been irreversibly damaged (Berry and Osgood, 1974). In addition to this, the small amount of cadmium that is

eliminated from the body must leave *via* the kidneys, further damaging them. As far as cadmium poisoning is concerned then, the adage "prevention is better than cure" is especially applicable, as cures for cadmium-induced diseases are, as of yet, non-existent.

An interesting complication in the case of acute oral cadmium intoxication is that it has frequently been (initially) misdiagnosed. This is largely because the symptoms are similar to those caused by microbial food poisoning (Table 1·3) although Physicians' awareness has also been questioned (Berman, 1980; Jenner and Cuningham, 1944). It is also worth noting that many of the chronic effects listed in Table 1·3 are not observed in acute cases because the subject dies before the effects have time to develop.

At the cellular level, cadmium (Cd^{2+}) competes with calcium, copper, iron and zinc for binding sites (Venugopal and Luckey, 1978). It follows that absorption of excess cadmium can cause symptoms reminiscent of dietary deficiencies of these metals (Yasumura *et al.* 1980). Conversely, dietary intakes of calcium, copper, selenium, zinc, ascorbic acid and/or vitamin D which exceed bodily requirements can ameliorate the effects of cadmium poisoning (Sugawara, 1989; Spivey-Fox, 1988; Waldbott, 1973). Intra-cellular ligands to which cadmium has a strong affinity include carboxyl, cysteinyl, hydroxyl, hystidyl, phosphatyl and sulphydryl groups. Enzymes containing these groups are inhibited by cadmium (Berman, 1980).

The absorption of cadmium by the body and its subsequent toxicity depend on its speciation(s) (Oldiges *et al* . 1989). Orally administered cadmium-thionein is not absorbed by rats to the same extent as cadmium chloride (Klassen *et al.* 1986). Recent toxicological research has examined such areas as the mechanisms of cadmium's nephrotoxicity (Goyer, 1989); the binding of cadmium by DNA (Serge, 1989); and cadmium-induced testicular dysfunction, hypertension, lung destruction and liver breakdown in rats (Sugawara *et al.* 1989; Balaraman *et al.* 1989; Olidges *et al.* 1989; Tseng *et al.* 1988).

1·5 The aims, scope and layout of this thesis

The aims of this thesis have been to gather and interpret information in two areas: 1. the concentrations of cadmium in the environment , and 2. the chemistry of cadmium in the environment. The *environment* has, for practical reasons, been largely limited to the city of Christchurch, New Zealand.

Studies in the concentrations of cadmium are of interest for the following reasons :

1. to determine whether or not the current concentrations of cadmium are a cause for concern (insofar as constituting a chronic health risk to groups within the non-occupationally exposed population);
2. to identify sources of cadmium in the environment and other factors which influence the metal's environmental distribution;
3. to create a data base which can be referred to in future studies.

This aspect of the project was tackled in terms of a series of surveys. Three of these (looking at aerosols, river water and tree leaves) were designed to monitor seasonal

variations of cadmium concentrations in each medium, and four (examining dust and soil, house-dust, household items and food) were "one-off" (unrepeated) in nature. The results of the seven surveys occupy the first "half" of this thesis (Chapters 3–9). In terms of human populations the scope of this research project is usually limited to persons not occupationally exposed to cadmium.

The chemistry of cadmium in the environment is of interest because it determines cadmium's availability and toxicity to human populations (section 1·3·2). The following topics were chosen for study: the adsorption characteristics of cadmium on a Christchurch soil (Chapter 10); the rainfall-induced mobility of cadmium in soil (Chapter 11); an assessment of a commonly used sequential extraction method for determining the speciations of cadmium in soil (Chapter 12); the weathering characteristics of galvanized-iron and of a surface coated with a cadmium-based paint (Chapter 13); and studies of cadmium's speciations in dust, soil, water and plastics (found in Chapters 3–5 and 9). With the exception of the speciation studies of dust, soil, water and plastics, studies of cadmium's chemistry are grouped together in the second "half" of this thesis, commencing at Chapter 10.

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CHAPTER 2
CADMIUM IN NEW ZEALAND

Overview

This chapter is a literature review of cadmium-related research in New Zealand. Research undertaken outside New Zealand but with a direct bearing on New Zealand studies is mentioned in some cases. Section 2·1 covers the distribution and sources of cadmium in the New Zealand environment, section 2·2 the cadmium intake of New Zealanders, and section 2·3 other research.

2·1 Cadmium in the New Zealand environment

2·1·1 Natural distribution

No systematic, New Zealand-wide survey has been undertaken to determine trace-element distribution patterns in rocks, soils, sediments or waters. The data that are available are primarily a result of the prospecting activities of private mineral exploration companies, although specific studies have been carried out by New Zealand Geological Survey and Chemistry Division, DSIR. Cadmium data, in particular, lack comprehensiveness (Braithwaite and Rabone, 1985).

Natural accumulations of cadmium are known to occur with the [lead-zinc-copper] sulphide mineral deposits of the Hauraki Goldfield, Coromandel Peninsula. Both naturally occurring forms of cadmium sulphide (greenockite and hawleyite) have been discovered in the Champion vein of the Tui Mine, Mount Te Aroha (Ansin, 1975). Sphalerite (ZnS) in the same mine contains about 0.6% cadmium (Ker and Wodzicki, 1983). Smaller quantities of cadmium are probably associated with the galena (PbS) chalcopyrite (CuS) and other copper-mineral deposits found in the Tui Mine (Ansin, 1975). Other locations where accumulations of cadmium may occur are West Nelson (molybdenum-copper sulphide and lead-zinc sulphide deposits) and Great Barrier Island (galena, sphalerite, chalcopyrite and bornite deposits) (Braithwaite and Rabone, 1985).

The average cadmium concentration in New Zealand subsoil has been estimated to be about 0.2 $\mu g\ g^{-1}$, although no derivation was given with this figure (Smith, 1984 and 1985). Stewart (1989) measured heavy metal levels in soils from 14 rural and remote sites on the Canterbury Plains, and reported cadmium concentrations ranging from 0.039 to 0.345 $\mu g\ g^{-1}$, with a mean value of 0.12 $\mu g\ g^{-1}$; concentrations on the low end of the range of values typically reported overseas.

Volcanoes are believed to be the principal natural source of atmospheric cadmium (Steiner and Clarkson, 1985) although as far as this author is aware, no actual experiments have been carried out to confirm whether or not this assumption is true in the case of New

Zealand's atmosphere. Sea-salt spray, a significant natural source of cadmium (Nriagu, 1989) may well contribute more to New Zealand's atmospheric cadmium burden than volcanoes, due to the country's extensive coastline compared with land area.

Background levels of cadmium in New Zealand freshwaters can be very low by world standards. The usual concentration in the upper reaches of the Manuherikia River, Central Otago, has been determined as 0.010 $\mu g\ l^{-1}$. Further downstream the river passes through grazing lands; here cadmium concentrations were found to increase slightly to 0.015 $\mu g\ l^{-1}$ (Ahlers and Hunter, 1988; Ahlers and Hunter, 1984; Hunter, 1981).

The geochemistry of cadmium in New Zealand ocean waters has been studied by Hunter (1982) and Hunter and Ho (1984). Surface concentrations were extremely low—about 0.001 $\mu g\ l^{-1}$. Dissolved cadmium and phosphate concentrations increased with depth and were highly correlated, inferring that cadmium was incorporated into living surface organisms during photosynthesis or grazing, and released gradually from sinking dead organisms by bacterial oxidation.

2·1·2 Anthropogenic inputs

2·1·2a Cadmium in the workplace

Cadmium levels in the workplace are monitored from time to time by the Toxicology Section of the Occupational Health Service, Department of Health, " ...whose work involves assessing risks associated with the use of commercial, household and agricultural poisons." (Anon. 1984a). Much of this work is, for reasons of confidentiality, unpublishable (Graham, 1985).

Graham (1980) surveyed eight cadmium-consuming factories in the Auckland area. In most cases, the forms of cadmium used were unlikely to cause intoxication (liquids, pastes and metallic cadmium). Precautions against (more toxic) airborne cadmium dusts were deemed "adequate", and at the two factories where air samples were taken (an electroplater and a PVC manufacturer) concentrations in the air were low ($<0.001\ mg\ m^{-3}$). However, the ingestion of cadmium-containing material through poor personal hygiene was identified as a potential health risk among workers. In addition to this, only one of the eight companies surveyed ran an ongoing safety education program.

Sharma (1981) detected high concentrations of cadmium in blood and urine samples from New Zealand agricultural workers who were occupationally exposed to cadmium-containing phosphate fertilizers. Blood cadmium levels as high as 14.66 $\mu g\ l^{-1}$ —eight times those of the control group—were found in exposed workers. Despite this, no symptoms of acute or subacute cadmium intoxication were observed in this case.

2.1.2b Cadmium in the urban atmosphere

Stewart (1989) showed, using a network of aerosol deposition collectors over the Canterbury Plains (which radiate out from Christchurch), that the deposition rate of cadmium from the atmosphere ($\mu g\ m^{-2} day^{-1}$) decreased exponentially ($p<0.001$) with increasing distance from the city of Christchurch, implying that the city was a large composite source of

cadmium. Deposition rates at urban, rural and remote locations were 4-6, 0.3–0.6 and 0.0058 μg $m^{-2}day^{-1}$, respectively. Soil cadmium levels at urban sites were enriched sevenfold over those at rural and remote sites.

Stewart *et al.* (1988) also measured the concentrations of five heavy metals in Kahikatea (*Dacrycarpus dacrydiodes*) ring wood from Riccarton Bush, Christchurch, for the purpose of gauging historical trends in the urban atmospheric heavy-metal burden. Cadmium levels in the urban wood diverged from those in background wood (taken from a site in South Westland) and increased steadily after about 1950. This trend was thought to reflect an increasing concentration of cadmium in the urban atmosphere with time.

The burning of coals during the winter months could be responsible for part of this increased burden, and in this respect it is worth noting that two groups have measured heavy metal levels in New Zealand coals. Sim and Lewin (1975) determined a New Zealand average coal cadmium concentration of 0.5 μg g^{-1}, after studying samples from 23 mines. Some of their calculations were questioned by Aggett (1983). More recently, Lynskey *et al.* (1984) examined five Waikato coals. These had a far lower cadmium content than most coals, a typical value being 0.02 μg g^{-1}.

2·1·2c The effect of traffic

The relationship between traffic and urban cadmium concentrations has been studied both in Auckland and Christchurch. Ward *et al.* (1977a) found the level of cadmium in soil near the Auckland Motorway to be significantly higher than that of background soil. The highest concentrations were associated with the greatest traffic densities. In contaminated soils the cadmium concentrations decreased with soil depth, indicating surface deposition of the metal.

In Christchurch, Fergusson *et al.* (1980) discovered a correlation between lead and cadmium levels in roadside dust, again implying a link between cadmium levels and traffic density. A mean cadmium concentration in the dust of 2.0 μg g^{-1} was reported. In a later study the concentrations of eight metals in roadside dust from 20 Christchurch sites were determined, monthly for nine months (Fergusson and Simmonds, 1983). The overall mean cadmium concentration in the dust was 1.46 μg g^{-1} and monthly means ranged from 1.01 to 2.01 μg g^{-1}, making cadmium the second most enriched element of those measured (lead was the most enriched). Rainfall significantly reduced the cadmium levels in roadside dust.

Fergusson and Ryan (1984) determined the concentrations of 26 elements in road-dust from five cities worldwide. Dust from Christchurch, Halifax (Canada) and Kingston (Jamaica)—three small cities—contained significantly lower concentrations of cadmium than dust from London and New York (large cities). Concentrations of cadmium in the Christchurch road-dust (ranging from 0.8 to 1.1 μg g^{-1}) were 4–14 times lower than concentrations in dust from New York, and 5–10 times lower than concentrations in London dust. Once again, cadmium and lead levels were found to be significantly correlated. The concentration of cadmium generally decreased with increasing particle size.

Cadmium in automotive emissions is thought to originate from cadmium-contaminated zinc compounds. These are used in lubricating oils (*e.g.* zinc dithiophosphate) and can be used for vulcanizing the rubber of car tyres (*e.g.* zinc oxide) (Lagerwaff and Specht, 1970).

2·1·2d The estuarine environment

Cadmium (and other environmental contaminant) levels in the livers and kidneys of five species of birds shot and collected from seven estuarine areas were determined by Turner *et al.* (1978). The areas were: Awarua Bay, Bluff; Avon-Heathcote Estuary, Christchurch; Hokitika River mouth, Hokitika; Hutt River, Lower Hutt; Kaituna River basin, Tauranga; and Manakau Harbour, Auckland. Concentrations of cadmium ranged from 0.05 $\mu g\ g^{-1}$ (wet weight) in the kidney of a pukeko (*Porphyrio porphyrio melanotus*) to 14.75 $\mu g\ g^{-1}$ in the kidney of a red-billed gull (*Larus novaehollandiae scopulinus*). The low levels found in the pukeko were ascribed to the bird's vegetarian habits. The authors concluded that comparison of metal concentrations between estuaries showed little evidence of heavy metal pollution in the estuaries near the most industrialized areas (Auckland, Hutt Valley, Christchurch).

More recently, Roper *et al.* (1988) arrived at a different conclusion regarding cadmium contamination in estuarine areas of the Auckland region, when they measured cadmium (and other pollutant) concentrations in sediment cores taken from five intertidal mudflats of Manukau Harbour. High surface sediment cadmium, copper, lead, zinc and hydrocarbon levels were found in sites not receiving direct discharges of those pollutants, and were thought be a result of surface runoff. Small opportunistic species and long-lived hardy species comprised most of the mudflat fauna at these sites. However, only at the most heavily contaminated site was there an apparent depletion in the numbers of species and individuals.

Millhouse (1975, 1977) determined the tissue cadmium content of seven organisms taken from the Avon-Heathcote Estuary, Christchurch. Levels as high as 52.51 $\mu g\ g^{-1}$ (dry weight) were reported in *Melagraphia aethiops*, a gastropod. The mud-flat snail (*Amphibola crenata*) had a mean cadmium content of 3.39 $\mu g\ g^{-1}$ and a maximum level of 8.85 $\mu g\ g^{-1}$. In a more recent study (Anon. 1988, Christchurch Drainage Board) a lower mean value of cadmium in the same organism (1.21 $\mu g\ g^{-1}$ dry weight) but a similar maximum concentration (8.22 $\mu g\ g^{-1}$) were determined. A comparison of concentrations found in Avon-Heathcote Estuary snails with those found in snails from Saltwater Creek Estuary (Ashley River mouth, North Canterbury)—an estuary designated "uncontaminated"—revealed that one-third of the former estuary's snails contained slightly more cadmium. This probably reflected the effect of urbanization on Christchurch's estuary.

Relatively high concentrations of cadmium have been found in the sediments of the industrially-flanked Heathcote River (which drains into the Avon-Heathcote Estuary) by Tan (1979) and also by Purchase (1983) in the vicinity of a lead-accumulator battery factory. Cadmium levels in the sediments of the estuary itself have been reported as lying within the

range 0.01 to 0.10 μg g^{-1} by Tan (1979) having a mean value of 1.19 μg g^{-1} by Millhouse (1975) and always being less than 0.5 μg g^{-1} by Anon. (1988) of the Christchurch Drainage Board. The result of Millhouse has been questioned (Tan, 1979; Robb, 1987; Fergusson, 1989). Excluding that result, absolute cadmium concentrations in the estuarine sediments are apparently low. Heavy metal (including cadmium) levels in the Avon-Heathcote and Saltwater Creek Estuaries are currently under investigation by Deeley (1989).

2·1·2e Cadmium in agriculture

In 1973 Williams and David, two Australian researchers, found high concentrations of cadmium in Australian phosphatic-fertilizers. Superphosphate, of the type commonly used for aerial crop-dusting in New Zealand, contained 38–48 μgCd g^{-1}. This generated some concern (Nielsen and Nathan, 1975; Dick *et al.* 1978). Roberts *et al.* (1976) studied the long term effect of applying superphosphate fertilizer to Papatoetoe silt loam, and found no evidence of a "measurable change in the total cadmium content of the soil." However, ten years later Rothbaum *et al.* (1986) arrived at a different conclusion. In their study, cadmium had been applied at a rate of 20 g $ha^{-1}yr^{-1}$ for 30 yr to a Papatoetoe clay loam. After this time about half the applied cadmium had accumulated in the top 22.5 cm of soil. Uptake of cadmium by clover pasture was estimated to be 0.4 g $ha^{-1}yr^{-1}$, or 2% of that applied.

Syers *et al.* (1986) characterized ten types of phosphate rock. Cadmium concentrations ranged from 2 μg g^{-1} in Chatham Island phosphorite to 100 μg g^{-1} in Nauru Island phosphate rock. Disconcertingly, in 1986 the latter variety constituted 40% of the phosphate rock used for fertilizer manufacture in New Zealand and Australia.

In addition to the problem of cadmium from phosphatic-fertilizers accumulating on farmland, wastewater from New Zealand fertilizer works can contain high levels of cadmium—up to 30 μg l^{-1} (Smith, 1984).

Compared with that of phosphatic fertilizers, and by world standards, the cadmium content of New Zealand sewage sludges has in the past been (apparently) low. The concentrations of the metal in dried sludge from Christchurch (Templeton) and Auckland (Manakau Purification Plant) have been given as 0.06–0.43 μg g^{-1} and 4.5 μg g^{-1}, respectively (Quin and Syers, 1978; Wells and Whitton, 1979). Quin and Syers (1978) found no evidence of cadmium accumulation in soil irrigated for 16 yr with treated sewage effluent (Templeton effluent; 840 mm yr^{-1} over 0.8 ha). Similarly, Wells and Whitton (1979) found no "significant" uptake of cadmium by plants grown in a (Manakau) sewage sludge/soil mixture.

2.1.2f The effect of mining

The Tui Mine, in Mount Te Aroha on the Coromandel Peninsula, was worked for a short period last century for gold, and again from 1966–1975 for lead, copper and zinc (Ansin, 1975; Hendy, 1981). Its geochemistry and geomorphology are described by Weissberg and Wodzicki (1970), Ansin (1975) and Ker and Wodzicki (1983).

Contamination of the environment by the mine has been examined by three parties. Ward *et al.* (1976) found that wind-borne dust from the mine caused high concentrations of cadmium in nearby soils, plants, stream sediments and waters; with the characteristic point-source pattern of decreasing concentrations with increasing distance from the mine. Soils 30 m from the treatment plant contained up to 50 μgCd g^{-1}. Twelve months after the mine's closure there had been a 25% decrease in the average soil cadmium concentration of a nearby pasture, which was attributed to leaching of cadmium through the soil (Ward *et al.* 1977b). Plants also showed a significant decrease in cadmium levels after 12 months.

Hendy (1981) noted that during the mine's operation, 1 000 000 m^3 of mineral-rich tailings had been deposited in a tailings pond located below the mine on the slopes of Mount Te Aroha, and that seepage from the tailings was flowing into Tui Stream. The discharge from the tailings contained 80-140 μgCd l^{-1} and the water of Tui Stream 20-25 μgCd l^{-1}. This was of concern because Tui Stream was at the time contributing to the domestic water supply of the Borough of Te Aroha.

Tunnicliff and Beaumont (1984) measured trace metal concentrations in streams and sediments from 21 locations throughout the Coromandel Peninsula. Cadmium levels in the three streams receiving direct discharges from mine workings were considerably higher than baseline levels. Of these, Tui Stream contained the most cadmium—up to 20 μg l^{-1}, a figure that compares well with Hendy's result. A correlation existed between cadmium concentrations in stream waters and those of their associated sediments.

2.1.2g Cadmium in other aquatic systems

Stoffers *et al.* (1986) assessed the extent of heavy metal pollution in Wellington Harbour and Waiwhetu Stream, by analysis of the <20 μm fraction of the marine and stream sediments. Cadmium levels in Wellington Harbour sediments were low, except in the Pencarrow outfall and Lambton Harbour areas. Concentrations at 17 sites in the Waiwhetu Stream, near an industrial area, ranged from <0.3 to 25.8 μgCd g^{-1}. Overall, the Harbour and Stream were considered to be "moderately to strongly" polluted with cadmium.

Timperley (1979) measured the concentrations of 15 metals in waters flowing from each of eight hydroelectric reservoirs on the Waikato River. In the case of cadmium, he concluded that the range of concentrations in Waikato River water (0.1–1.2 μg l^{-1}) did not differ significantly from values typically reported for freshwaters.

Low levels of cadmium are found in New Zealand geothermal waters, used for power production. Waters from wells at Wairakei field have been estimated to contain 0.5 μg Cd l^{-1} by Ellis (1978) but only about 0.01 μg Cd l^{-1} by Goguel (1988). Waters from the Broadlands field also contain about 0.01 μg Cd l^{-1} (Ellis and Mahon, 1977; Goguel, 1988).

A small amount of data is available detailing the cadmium contents of dump leachates. Smith (1984) gives figures of 5 μg l^{-1} for leachate from the Hutt City (Silverstream) dump, and 10–50 μg l^{-1} for leachate from Auckland's "Tip F".

On one occasion in 1966, New Zealand rainwater (collected in 1964) was reported to contain small amounts of the radioactive isotope cadmium-109, presumably formed during "Starfish Prime", a high altitude nuclear detonation carried out over Johnston Island on July 9, 1962 (McCallum and Woodward, 1966). The actual concentration of cadmium-109 in the rainwater was unspecified.

2·2 Cadmium in New Zealand food and in New Zealanders

2·2·1 Dietary intakes

Guthrie (1975) analysed 130 different New Zealand foods for five trace elements. Although oysters contained up to 5.01 μg g^{-1} (wet weight) cadmium, most foods analysed were in the range 0.01-0.05 μg g^{-1}, resulting in a estimated intake (said to be) well below the World Health Organization's provisional tolerable limit of 400–500 μgCd $week^{-1}$ (the actual intake figure was not given). Other than oysters, the highest concentrations of cadmium were found in liver, kidney, wheatbran, wheatgerm, "farex", soybean flour, canned mackerel, marmite and some condiments. Root vegetables had higher levels than other vegetables.

Guthrie and Robinson (1977, 1978) then conducted a *duplicate diet* survey, involving 23 Dunedin women (age range 19-50 yr) who chose 179 diets. The womens' mean daily cadmium intake was estimated to be 21±14 μg, again well within the World Health Organization's recommended limit of 60–70 μgCd day^{-1}.

Since then, three *total diet* surveys have been carried out by researchers at Chemistry Division, DSIR, working in conjunction with the Department of Health. These were undertaken on behalf of the Department of Health's "Health Protection Programme", designed to regularly monitor the levels of heavy metals and pesticide residues in foods (Hannah *et al.* 1988).

The first of these involved measuring the concentrations of 13 trace elements in eight composite food samples (Dick *et al.* 1978). Food was collected from Auckland, Wellington, Christchurch and Dunedin. The estimated daily cadmium intake was 16 μg assuming 3.3 kg of food was eaten (high energy diet), or 12 μg for 2.5 kg of food (more normal diet). These figures agree reasonably well with Guthrie and Robinson's (1977) estimate of 21±14 μgCd day^{-1}. Comparison with Canadian (93 μgCd for 2.5 kg food) and American (32 μgCd for 2.5 kg food) figures suggested that New Zealanders were ingesting significantly less cadmium.

In the second such study, Pickston *et al.* (1985) measured the concentrations of 20 elements in nine composite samples, also agglomerated from food collected from the four main centres. This survey was designed to take into account changes in the New Zealand diet that had occurred since the survey of Dick *et al.*, such as an increased consumption of vegetable oil, margarine, wine and instant foods. A daily cadmium intake of 71 μg for 3.3 kg of food (54 μg for 2.5 kg of food) was calculated—a fourfold increase on the 1978 estimate of Dick *et al.* Oysters were thought to be responsible for about 33 μg of the 71 μg

total daily intake, and the "oyster effect" was forwarded as a partial explanation for the apparent increase. However, Dick *et al.* also analysed shellfish (type unspecified). Even without oysters, a greater than twofold increase would be observed. Notwithstanding this, the authors concluded "...there should be no concern over the [cadmium] levels found in this survey."

The results of the third Department of Health-sponsored total diet survey, completed by 1989, have not yet been published. This survey was more comprehensive than the previous two, as it involved the measurement of heavy metal levels in individual food items (rather than in composite samples) (Hannah *et al.* 1988).

2·2·2 Cadmium in individual foods

2·2·2a Infant foods and dairy products

Casey (1977) analysed 35 different infant food items for seven trace metals. Cadmium concentrations were low in all samples, the highest being 0.04 μg g^{-1} in *Sobee*, a soybean-based powder. A pooled sample of human milk (from 25 mothers) and homogenized cow's milk contained <0.001 and 0.003 μgCd ml^{-1}, respectively; both values lower than those reported overseas for the same materials. The Department of Health has also expressed interest in conducting a survey of infant foods (Hannah *et al.* 1988).

MAFQual, a branch of the Ministry of Agriculture and Fisheries, is responsible for monitoring heavy metal levels in dairy products. No "significant" levels of cadmium were found in dairy products during the 1987/1988 season (Morrison, 1988). Protein products were reported to contain <0.01 μgCd g^{-1} and milkpowder 0.08–0.3 μgCd g^{-1}.

2·2·2b Meat and fish

The quality of samples of the 800 000 tons of meat exported annually is monitored at the Wallaceville Animal Research Centre, also a division of the Ministry of Agriculture and Fisheries. Cadmium concentrations have frequently exceeded the maximum tolerance limit of 1 μg g^{-1} in the kidneys of cattle, sheep, wild pigs and wild deer (Clear, 1988). This is not surprising, as cadmium accumulates in the kidneys. Concentrations in cattle, pig and sheep muscle meat have typically been below 0.05 μg g^{-1} (Solly *et al.* 1981).

Brooks and Rumsey (1974) measured the heavy metal content of eight species of commercially important marine fish (gurnard, hapuku, kahawai, kingfish, moki, snapper, tarakihi and trevally). Seventy samples of each species were taken. Cadmium levels in the flesh of the fish were low, ranging from 0.002 to 0.02 μg g^{-1} (wet weight). However, concentrations in the soft organs of several species exceeded the legal limit of 1 μgCd g^{-1}, the highest figure being 12.15 μgCd g^{-1} in the liver of a hapuku (*Polyprion oxygeneios*). The authors noted that the soft organs would not normally be consumed by humans, and that dilution would occur in the case of fishmeal production.

Brooks *et al.* (1976) then examined the heavy metal burden of freshwater fishes living near geothermal areas. A total of 115 specimens of rainbow trout (*Salmo gairdneri*) and brown trout (*Salmo trutta*) were successfully lured from various lakes and rivers on

North Island's Volcanic Plateau. Edible tissue cadmium levels were about 10 times higher than those of marine fish, but still low (mean level 0.06 $\mu g\ g^{-1}$). The highest levels of cadmium were found in the gills; the lowest in the flesh and the gonads.

Gauldie and Nathan (1977) determined the concentrations of six metals in the otoliths of 1 076 tarakihi (*Cheilodactylus macropterus*) and reported that cadmium "did not occur in significant quantities."

2·2·2c Oysters and other shellfish

This topic has been widely studied, due to the pronounced ability of some shellfish to accumulate large quantities of cadmium. Brooks and Rumsby (1965) first demonstrated this phenomenon, when they determined the natural concentrations of 11 elements in an oyster (*Ostrea sinuata*) a mussel (*Mytilus edulis aoteanus*) and a scallop (*Pecten novae-zelandiae*) dredged from Tasman Bay. Cadmium levels in the soft portions of the scallop and oyster were very high, mean levels being 246 $\mu g\ g^{-1}$ and 35 $\mu g\ g^{-1}$, respectively. Biological enrichment factors (relative to seawater) were estimated to be $2{\cdot}26 \times 10^6$ for the scallop and 3.18×10^5 for the oyster. Almost all the cadmium in the scallop was located in the organism's stomach (mean level 2000 $\mu g\ g^{-1}$) whereas in the oyster, cadmium was more evenly distributed. Further experiments revealed that the oysters absorbed cadmium steadily from a spiked seawater solution until a threshold tissue concentration of between 40 and 140 $\mu g\ g^{-1}$ was reached, when uptake ceased (Brooks and Rumsby, 1967). This was thought to indicate unselective cadmium absorption, probably by coordination to organic ligands. The highest concentrations of cadmium in the oysters were found in the gills; the lowest in the white and striated muscle.

The effect of depth on the heavy metal content of commercially-grown green-lipped mussels (*Perna canaliculus*) was investigated by Nielsen (1974). Mussels were cultured in seawater on 9 m ropes suspended vertically from floating rafts. At Kenepuru Sound, a sheltered site, the cadmium content of the mussels increased with depth, whereas at the more exposed location of Waiheke Island, depth had no effect on the concentrations. Neilsen attributed the dissimilarity of the results to differences in the mixing of the water columns between the two sites; resulting, for example, in variations in metal concentration gradients and the type of food organism with depth. Cadmium concentrations in the mussels did not exceed 0.7 $\mu g\ g^{-1}$ (wet weight).

The first comprehensive survey of heavy metal concentrations in New Zealand molluscs was that of Nielsen and Nathan (1975). Samples of 13 molluscan species were collected from a total of 199 locations. Confirming the earlier work of Brooks and Rumsby (1965) the highest cadmium level (329 $\mu g\ g^{-1}$) was found in the scallop (*Pecten novaezelandiae*) stomach. Concentrations in excess of 3 $\mu gCd\ g^{-1}$ in oysters were "not uncommon". At the time, the New Zealand Food and Drug Regulations set the upper limit of cadmium allowable in all food at 1 $\mu g\ g^{-1}$. Of the 13 species examined, and in addition to the scallop, this limit was exceeded by the dredge oyster (*Ostrea lutaria*) the saddle oyster (*Anomia walteri*) and the rock oyster (*Crassostrea glomerata*); with mean wet weight

cadmium levels of 3.9, 2.0 and 1.3 μg g^{-1}, respectively. In a later study, dredge oysters from Foveaux Strait were found to contain up to 9 μgCd g^{-1} (Neilsen, 1975). The geographic distribution of oysters with high cadmium concentrations and the pattern of prevailing currents suggested that the source of cadmium (presumably natural) lay to the west of Foveaux Strait, possibly in Fiordland.

Winchester and Keating (1980) determined the concentrations of 11 trace metals in North Island farmed oysters. Although a mean level of 0.63 μgCd g^{-1} was found, one quarter of the oysters contained more cadmium than the legal limit (1 μg g^{-1}).

McKenzie (1981) calculated that the cadmium intake of Bluff residents, some of whom were rumoured to eat several dozen oysters daily for up to six months of the year, could exceed the World Health Organization tolerable intake by 6–7 times. However, she also noted that "Examination of the health statistics for the area has not revealed any suggestion of a detrimental effect from a high intake of cadmium...". Sharma *et al.* (1983) measured blood cadmium levels in a group of 78 oyster-eating individuals, and found that they were on average about four times higher than blood cadmium concentrations in a control group (n = 17). Concentrations of cadmium in the blood of the oyster consumers increased steadily during the first half of the oyster season, and remained relatively constant thereafter.

Speciations of cadmium in Foveaux Strait dredge oysters were investigated by Sharma (1983). Most (75%) of the cadmium was found in the particulate fraction in the tissue and bound to high molecular-weight proteins in the cytosol; 25% of it was associated with low molecular-weight proteins (M_r 6 000–12 000) similar in volume to rat metallothionein but which, unlike rat metallothionein, did not bind zinc. The association of cadmium with a metallothionein-like protein was of concern because cadmium-thionein administered orally had been shown to be substantially more damaging to intestinal cells than other forms of cadmium. The average cadmium content of dredge oysters in this study was 5.8 μg g^{-1} (wet weight), again well above the legal limit.

Timperley (1984) measured the cadmium content of pacific oysters (*Crassostrea gigas*) and rock oysters from Manakau Harbour, Mahurangi Harbour and the Bay of Islands. Pacific oysters contained less cadmium (mean value) than rock oysters at all sites, and samples of both species from Mahurangi Harbour had higher levels than oysters from the Bay of Islands. Mean cadmium concentrations ranged from 0.19 μg g^{-1} (wet weight) in pacific oysters from the Bay of Islands (Orongo Bay) to 1.29 μg g^{-1} in rock oysters from Mahurangi Harbour (Pukapuka Inlet).

New Zealanders continued to ingest illegal oysters until 1984—when the law was changed. The new regulations set the cadmium limit at 1 μg g^{-1} in all foods except shellfish (Anon. 1984b). No limit was set on the permissible level in shellfish. Although this move afforded a measure of protection to the developing oyster-farming and established oyster dredging industries, future events may prove it to have been unwise, especially if an increased consumption of oysters is concomitant with the emergence of the oyster-farming industry. Specifically, an increase in oyster consumption would lead to a greater possibility of chronic cadmium intoxication occurring in an individual after 30–40 years.

Cadmium speciations in New Zealand oysters have also been studied in Sweden, by Nordberg *et al.* (1986), who found using gel filtration that whereas cadmium in dredge oysters (from Foveaux Strait) was bound to proteins similar in molecular-weight to vertebrate metallothionein (M_r *ca.* 6 500), cadmium in rock oysters (from Waiheke Island) was associated with polypeptides with molecular-weights of about 1 000. Cadmium-binding proteins in the dredge oyster exhibited the heat stability and affinity for cadmium typical of vertebrate metallothionein, but were less reactive than it in a competitive binding radioimmunoassay. (The protein may or may not have been a metallothionein; full characterization would have required amino-acid sequencing). Concentrations of zinc, a metal which can ameliorate the effects of cadmium intoxication by competitive absorption, were lowest in the dredge oyster, the species with the most cadmium. Mean levels were 5.3 $\mu gCd\ g^{-1}$ and 100 $\mu gZn\ g^{-1}$ (wet weight) in the dredge oyster; and 1.4 $\mu gCd\ g^{-1}$ and 936 $\mu gZn\ g^{-1}$ in the rock oyster. The results of Nordberg *et al.* agree well with those of Sharma (1983).

2·2·2d Cigarettes, casserole dishes and printed matter

Brooks and Trow (1979) analysed 49 New Zealand and 13 overseas brands of cigarettes for lead and cadmium. The mean cadmium content of the New Zealand brands ranged from 0.23 to 0.56 $\mu g\ g^{-1}$ (mass at 60% relative humidity) with most being present in the tobacco rather than in the paper. *Low tar* brands contained the least cadmium. The authors noted that although cadmium levels were comparatively low in New Zealand brands, lower levels were desirable.

Public interest in cadmium's toxicity received a boost in 1974, when the Consumers' Institute of New Zealand tested 15 brands of enamelware casserole dish for the amount of cadmium leached into solution under simulated cooking conditions (Anon. 1974). Only two of the brands complied in this respect with legal specifications. The most cadmium was leached from French-made casseroles, which released up to 21 times the legal limit of 0.7 $\mu gCd\ ml^{-1}$. Cadmium was present in the enamel of the casserole dishes as red, orange and yellow pigments.

Bathurst (1977) examined the leaching of cadmium from printed matter (comics, rag and plastic books, food wrappers, play materials) to which children were commonly exposed. No cadmium was extracted from the items concerned under simulated cooking conditions.

2·2·3 Acute cadmium poisoning from food

Sixty-two New Zealand airmen suffered acute cadmium poisoning in one incident during World War II, after drinking (acidic) fruit juice that had been prepared in a galvanized urn (Jenner and Cuningham, 1944). The juice leached cadmium from the urn's interior, and was later estimated to contain 200 $\mu gCd\ ml^{-1}$, each airman therefore ingesting an approximate dose of 56 mg Cd. The minimum lethal dose by ingestion is estimated to be 350 mg Cd (Yasumura *et al.* 1980). Poisoning was characterized by severe gastroenteritis. All the victims had recovered after three days.

2·2·4 Cadmium in New Zealanders

At birth, the body burden of cadmium in New Zealanders is, by world standards, low. Analysis of tissues from 39 deceased foetuses revealed a mean liver content of 0.07 μgCd g^{-1} (dry weight) and a mean muscle content of 0.03 μgCd g^{-1} (Casey, 1976; Casey and Robinson, 1978).

Following birth, the body accumulates cadmium with age, reaching an apparent maximum in the 60–80 yr age group (mean liver content for 10 subjects: 17.2 μg g^{-1}, dry weight) (Casey *et al.* 1981; Pickston *et al.* 1983). Accumulation was shown by Casey *et al.* (1981) to occur in the liver, heart, skeletal muscle and lung tissue.

Greater concentrations of cadmium have been found in the lungs and kidneys of deceased smokers, and in the blood of living smokers, than in those of control groups comprising (deceased or living) non-smokers (McKenzie, 1974; Sharma *et al.* 1983). Interestingly, Pickston *et al.* (1981, 1983) calculated that significantly more cadmium was present in the livers of Southlanders than in those of other New Zealanders, probably as a result of the former group's high oyster intake.

The wet weight range of cadmium in New Zealand livers was given as 0.3 to 6.9 μg g^{-1} by Johnson (1976) (11 subjects) and as 0.2 to 6.2 μg g^{-1} by Pickston *et al.* (1983) (96 subjects); figures which agree well. Cadmium tissue concentrations in New Zealand have been at the lower end of the range of values reported elsewhere (Pickston *et al.* 1983), even when the higher levels found in Southlanders are taken into account.

2·3 Other studies relating to cadmium

2·3·1 Metabolism and toxicology

Studies relating to the metabolism of cadmium in the rat have been carried out by Mason (1981, 1982, 1983, 1984). Accumulation and subcellular distribution of cadmium (administered intraperitoneally) in the liver of the neonatal rat was found to be age-dependent and not related to the total liver concentrations of copper, zinc, metallothionein, copper-thionein or zinc-thionein. Cadmium incorporated into the liver was initially associated with the high molecular-weight protein fraction but was gradually transferred to the low molecular-weight (metallothionein) fraction, the speed of the transfer process decreasing with age (Mason, 1982). Dimercaptosuccinic acid (intraperitoneally as 50 μg g^{-1} daily for 17 days) proved ineffective in remobilizing cadmium from the kidneys of cadmium-pretreated rats, due to the high affinity of the metal for metallothionein, but showed promise as a therapeutic means of removing liver-bound cadmium (Mason, 1981). In the course of investigating the renal metabolism of gold, Mason (1983) found that gold uptake by rat kidneys increased when the rats were pretreated with divalent cadmium (Cd^{2+}).

Roberts (1983a, 1983b, 1984) investigated cadmium-induced toxicological effects in *Escherichia coli* . Cadmium added to the growth medium ($CdCl_2$, 10 μM) increased both the time taken for growth and the susceptibility to radiation of *E. coli* . Partial protection against the effects of cadmium was afforded by prior growth of *E. coli* in a zinc (Zn^{2+}) containing

medium (Roberts, 1983a and 1983b). Unexpectedly, and in contrast to the effect of cadmium on radiation sensitivity, growth in a cadmium-containing medium was later found to induce a certain amount of heat resistance in *E. coli* (Roberts, 1984).

2·3·2 Uses of cadmium compounds

Standish (1964) assessed the feasibility of using a fusible cadmium alloy (Bi-Pb-Sn-Cd) as a substitute for high melting-point metals in the study of various transfer phenomenon (*e.g.* momentum, mass transfer, heat).

The electrical properties of monocadmium and dicadmium stannates ($CdSnO_3$ and $CdSnO_4$) were examined by MacKenzie *et al.* (1979a, 1979b) and Cardile *et al.* (1987). Polycrystalline pellets of both compounds showed small (but significant) photoelectrochemical effects, and could be utilized in energy conversion devices such as solar cells (MacKenzie *et al.* 1979a, 1979b). Yellow and green forms of dicadmium stannate were found to be crystallographically similar, yet have different electronic and spectroscopic properties (Cardile *et al.* 1987).

2·3·3 Studies in analytical methodology

Sharma *et al.* (1982) tested and described a "simple and accurate" method of determining the cadmium content of blood, urine and hair samples. Digestion was accomplished at low temperatures (70 °C) using small volumes (0.5-1.0 ml) of nitric or 1:1 nitric/sulphuric acids in closed digestion tubes. Subsequent analysis by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) showed good recoveries.

Goguel (1983) examined the means by which background correction in the Flame AAS analysis of cadmium from rock extracts could be improved. These involved:

1. dissolution of only part of the rock matrix but most of the cadmium by a simple nitric acid extraction, and
2. correction of the background absorbance at the cadmium 228.80 nm line with the signal received from the arsenic 228.81 nm line.

2·4 Conclusion

In New Zealand, cadmium has been studied intermittently, by various groups for various reasons; however, the overall picture is an interesting one. Although little is known about the natural distribution of cadmium in New Zealand, the element has been shown to be slowly accumulating in the urban, estuarine, agricultural and (to some extent) aquatic environments. Mining can produce substantial fluxes of cadmium over comparatively small areas, both when the mine is operative and after closure.

At present, the effect with the greatest potential to boost human intakes of the metal is probably cadmium's accumulation on farmland and uptake by crops (through the use of high-cadmium varieties of phosphatic-fertilizers), as food accounts for an estimated 90% of the body burden of the metal in a non-occupationally exposed population (section 1·4·2).

This effect could also, at some future date, damage the nation's meat export trade (section 2·2·2b).

In the past, New Zealand food has contained similar or smaller levels of cadmium than food consumed overseas, the exception being oysters. The current lack of any standard governing the permissable level of cadmium in oysters could lead to the development of chronic cadmium diseases in certain sub-groups of the population, especially if oyster intakes increase.

Tissue cadmium levels in adult New Zealanders have, in the past, been on the lower end of the range of values reported overseas. Higher levels are generally found in Southlanders than in other New Zealanders, probably due to the former group's higher oyster consumption.

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CHAPTER 3
A STUDY OF POINT SOURCES OF CADMIUM IN CHRISTCHURCH

3·1 Introduction

The effect of point-sources on urban cadmium levels has received little attention in New Zealand. Graham (1980) in his survey of eight Auckland factories (section 2·2·2a) mentioned that in several cases, cadmium-containing fumes were vented outside the factory walls and into the surrounding environment, but no measurements were made. Fergusson *et al.* (1980) found enhanced concentrations of cadmium in dust outside (6.8 $\mu g\ g^{-1}$) and 1.5 km downwind of (6.5 $\mu g\ g^{-1}$) a Christchurch tyre-manufacturing firm. Overseas, concentrations of cadmium in factory (and other point-source) emissions have in some cases been sufficiently high to directly threaten public health (Muskett *et al.* 1979; Harper and Sullivan, 1987).

Potential sources of cadmium in cities fall into two categories: those where cadmium is used intentionally and those where it is not. In the latter case, cadmium is a minor component of another material (zinc, for example). Table 3·1 is a list of potential sources of cadmium which were operational within Christchurch city at the time of this study.

Table 3·1

Potential sources of cadmium in Christchurch at the time of the dust and soil survey.

Potential source	Reason	Chapter and section reference
Cadmium electroplating	Cadmium compounds used	1·2·1
Ceramics production	Cadmium compounds sometimes used	1·2·1
Cement production	Incineration of cadmium-containing materials	1·3·1 (and Förstner, 1980)
Coal combustion	Cadmium in coal	2·1·2b and Chapter 7
Engineering and welding firms	Cadmium compounds sometimes used	1·2·1
Fertilizer manufacture	Cadmium in phosphate rock	2·1·2e
Galvanizing and weathering of galvanized products	Cadmium is associated with zinc	1·2·1
Lead accumulator battery production	Cadmium is associated with lead	1·2·1
Metal processors (non-ferrous)	Cadmium associated with copper, lead, zinc and various alloys	1·2·1
Plastics production	Cadmium compounds sometimes used	1·2·1
Spray painting firms	Cadmium compounds sometimes used	1·2·1
Tyre manufacturers and tyre wear	Zinc compounds sometimes used	2·1·2c

The primary aim of this section of the work was the identification and (partial) characterization of the point-sources of cadmium in the city of Christchurch, New Zealand. Source identification involved comparison of the cadmium concentrations in dust and soil samples taken from nearby the potential sources with the mean cadmium concentration of samples taken from suburban locations. Source characterization included:

1. examination of the effects of rainfall, wind direction and distance from the source on the cadmium concentrations in dust, and the effect of depth on the concentrations in soil;
2. measurement of the extent of correlation between the concentrations of cadmium and zinc, cadmium and lead, and cadmium and organic matter in soil and dust samples;
3. determination of the cadmium burden of various size and density fractions, and magnetic and non-magnetic fractions, of some dust samples.
4. electron microprobe and X-ray powder diffraction (hereafter XRPD) analysis of components of some dust samples.

3·2 Method

3·2·1 Collection and handling of samples

A total of 134 dust and 30 soil samples were gathered from 69 Christchurch locations; industrial, residential and background. Most samples were collected on various days in February, March, April and May 1987. Four dust samples were also collected on 11 February 1988. Dust and soil samples destined for sequential extraction (results given in Chapter 12) were collected on 17 January 1989. Dust samples outnumbered soil samples because the majority of industrial sites were surrounded by paved areas. In most cases, only one sample was taken at each location, but at some sites more extensive sampling was carried out in order to gauge the effects of wind direction, rainfall and distance on cadmium concentrations.

Residential sites were chosen to correspond with the eight principal compass directions relative to the central city. They were: Holly Road (N), Kim Street (NE), Worcester Street (E), Finlay Place (SE), Wembley Street (S), Lyttleton Street (SW), Rudleigh Avenue (W) and Kilsythe Place (NW). Their positions are shown in Appendix 3·1 (inside back cover). "Background" soil samples were taken from Gebbies' Pass (Port Hills) and from under two old Christchurch houses, one built in 1852 and the other in (about) 1900. Background dust samples were not collected, as it was assumed that no road-dust would be entirely free from the effects of automotive emissions (section 2·1·2c).

To measure the extent of variability between samples collected from the same site, 8 dust samples were gathered from a 5 m stretch of Blenheim Road, and a further 10 dust samples were taken from a 4 m^2 dust patch near Princess Street.

Soil cores (of 2.5 cm diameter) were obtained to a depth of 9 cm with the use of a stainless-steel core extractor. They were stored in clean plastic bags. After collection the soil cores were allowed to air-dry for a period of 48 hr. Dust samples were collected with a plastic brush and pan from footpaths, gutters and roadsides in relevant areas, and were also

stored in clean plastic bags. The area over which each dust sample was collected varied depending on the availability of dust, but generally did not exceed 0.5 m^2. The dust samples and air-dried soil cores were oven-dried for 48 hr at a temperature of 90–100 °C. It was verified that by following this practice the samples were dried to constant weight. Some of the soil cores were sectioned into 3 cm segments. Both dust and soil samples were then sieved, with particles finer than 563 μm being retained and placed in fresh plastic bags. Prior to sieving it was necessary to crush (taking care not to grind) the hardened soil cores using a heavy plastic-covered steel rolling-pin. After sieving, all samples were homogenized by vigorous shaking of the plastic bags at various angles.

Eleven dust samples found to contain high concentrations of cadmium were fractionated according to grain diameter, in order to determine the relative cadmium burden of each fraction. Each sample (typically 5–20 g) was divided into four fractions using nylon sieves of varying mesh size. The ranges of grain size in each fraction, and their designation under the Wentworth classification system (Lewis, 1981) were: 563–213 μm, mainly medium sand; 213–149 μm, fine sand; 149–62.5 μm, very fine sand; and <62.5 μm, silt and clay.

Portions of 8 of the 11 samples fractionated by size were also divided into five fractions based on density, using chloroform ($CHCl_3$) and tetrabromoethane (CH_2Br_4) in various proportions as flotation media. In each case about 10 g of dust was mixed with 50 ml of chloroform (density 1.47 g ml^{-1}) in a separating-funnel. Material less dense than chloroform was collected, washed with 1, 2 dichloroethane (density 1.25 g ml^{-1}), dried using an infrared heat-lamp, and weighed. Material more dense than chloroform was transferred (after washing) to another separating funnel. The process was repeated three times more using chloroform and tetrabromoethane in the ratios 60:40 (density 2.07 g ml^{-1}), 30:70 (density 2.52 g ml^{-1}) and 0:100 (density 2.97 g ml^{-1}). The five resultant density fractions were: <1.47 g ml^{-1}, 1.47–2.07 g ml^{-1}, 2.07–2.52 g ml^{-1}, 2.52–2.97 g ml^{-1} and >2.97 g ml^{-1}. During density fractionation, there is a possibility that some of the sample will dissolve; nevertheless, the technique is useful in the elucidation of overall trends in a metal's concentration with density (Hopke, 1985).

A magnetic fractionation of five dust samples was also carried out, with the use of a small permanent magnet covered with plastic for easy removal of the magnetic material. (It should be noted that designation of particles as magnetic or non-magnetic is entirely a function of the strength of the magnetic field used in their separation (Linton *et al.* 1980).)

In one case, an XRPD characterization (technique described in Chapter 14) was attempted on metallic-looking material isolated from the non-magnetic fraction of dust collected from outside a welding firm. Metallic fragments were separated from the rest of the sample with the use of a fine needle and a microscope. They were then glued to a glass slide (using an epoxy resin cement) and analysed over the two-theta angular range 20–100 °. The magnetic and non-magnetic fractions of the two dust samples with the highest concentrations of cadmium were also analysed using an electron microprobe, a technique which had the capability of detecting small (>1 μm) fragments of metallic cadmium

(described in Chapter 14). This analysis was carried out at the Department of Mechanical Engineering, University of Canterbury, by a staff member.

Measurement of the organic content of dust and soil samples was undertaken when sufficient material was available. Soil cadmium and organic levels have been found by previous researchers to be positively correlated (Gerritse, 1984; Pickering, 1980). Accurately weighed 1–10 g dust or soil samples were ashed overnight at 500 °C and the weight loss measured. The absolute value of the percentage weight loss of a sample was taken as (an approximate estimate of) that sample's organic content.

3·2·2 Digestion and analysis for cadmium, lead and zinc

For both the soil and the dust, between 0.5 and 1.0 g of each sample was boiled in 20 ml of 4 M nitric acid ("AnalaR" grade, BDH) for 30 minutes. After the liquid had cooled it was passed through a Whatman No. 540 filter paper, which had previously been washed twice with 4 M nitric acid and once with doubly-distilled water (DDW), directly into a volumetric flask. The residue was washed three times with DDW, and the filtrate diluted to 50 ml.

Concentrations of cadmium in these solutions were usually such that an absorbance within the range 0.1 to 0.6 was obtained upon atomization of a 2 µl sample in the Graphite Furnace Atomic Absorption Spectrometer (GFAAS). Samples with cadmium absorbances greater than 0.6 were either diluted and analysed by GFAAS, or in some cases analysed directly by Flame Atomic Absorption Spectrometry (FAAS).

All solutions were analysed on the same day as they were prepared, in order to minimize (potential) losses of cadmium through adsorption on the inner walls of the volumetric flasks (Chen and Zhang, 1984). The extraction efficiencies using nitric acid for cadmium, lead and zinc from road-dust samples have previously been estimated to be 100%, 98.9% and 98.6%, respectively (Fergusson and Simmonds, 1983).

The GFAAS furnace heating program used for the analysis of cadmium is given in Table 3·2.

Table 3·2

GFAAS furnace heating program for the measurement of cadmium in dust and soil extracts.

Step number	Step	Temperature (°C)	Ramp time (s)	Holding time (s)
1	Drying # 1	80	2	20
2	Drying # 2	120	5	5
3	Ashing	340	5	0
4	Atomization	2 000	2	2

The absorbance due to cadmium was monitored at a wavelength of 228.8 nm. Background absorbance was measured using a deuterium lamp, and was automatically

subtracted. The spectral band-pass (slit width) was set at 0.5 nm. It was found that by using the above parameters and furnace heating program (Table 3·2), sharp symmetric peaks were obtained for cadmium upon atomization, and memory effects were not observed. Other parameters relating to the use of the GFAAS are given in Chapter 14.

Lead and zinc (and in some cases cadmium) analyses were carried out by FAAS. Instrumental parameters used during the analyses of these metals by FAAS are given in Chapter 14.

Working standards in the range 0.001–6 $\mu g\ ml^{-1}$ cadmium, 2–40 $\mu g\ ml^{-1}$ lead, and 0.2–2 $\mu g\ ml^{-1}$ zinc were prepared by dilution from 1 000 $\mu g\ ml^{-1}$ stock solutions, and given the same acid strength as the sample solutions (1.6 M). Usually, 6–10 standards were used to construct any particular calibration curve. Preparation of the stock solutions, and precautions pertaining to contamination control (such as the acid-washing of glassware) are given in Chapter 14.

3·3 Results and discussion

3·3·1 Precision, bias and inter-sample variability of the results

Estimates of the precision of the analytical method were obtained by replicate analyses of five different samples; a soil sample from Gebbies' Pass (Port Hills), a soil sample from Halswell, Christchurch (Tai Tapu silt loam), a sample of Tai Tapu silt loam that had been spiked with 37 $\mu gCd\ g^{-1}$ (from a standard solution), a previously well-analysed road-dust sample, and a certified-reference sediment sample (SDN1/2; International Atomic Energy Agency, Vienna). Because the true concentration of cadmium was "known" in the last three cases, these samples were also used to estimate the degree of analytical bias (defined as the difference between the measured concentration and the true concentration). One or two reference samples were included with each batch of samples analysed. The results of these analyses are given in Table 3·3.

Table 3.3

Summary statistics relating to the repeated analyses of five different samples.

Sample	Number of analyses (n)	Given or assumed concentration ($\mu g\ g^{-1}$)	Mean concentration (this study) ($\mu g\ g^{-1}$)	Standard deviation (μg g-1)	Coefficient of variation[a] (%)	Error[b] on mean at 95% confidence level ($\mu g\ g^{-1}$)
Soil from Gebbies' Pass						
Cadmium	6		0.068	0.006	9.03	±0.005
Lead	6		34.1	1.5	4.42	±1.4
Zinc	6		56.8	8.5	15.0	±7.7
Tai Tapu silt loam (clean)						
Cadmium	14		0.163	0.017	10.0	±0.008
Lead	14		45.1	5.7	12.7	±2.8
Zinc	14		52.2	14.0	27.0	±6.9

Table 3·3 continued...

Sample	Number of analyses (n)	Given or assumed concentration (μg g^{-1})	Mean concentration (this study) (μg g^{-1})	Standard deviation (μg g-1)	Coefficient of variation[a] (%)	Error[b] on mean at 95% confidence level (μg g^{-1})
Tai Tapu silt loam (spiked)						
Cadmium	10	37.2[c]	37.2	2.3	6.05	±1.2
Road-dust (RM1)						
Cadmium	7	1.30	1.37	0.25	18.0	±0.20
Zinc	7	433	439	30	6.83	±5
Certified-reference sediment sample (SDN1/2)						
Cadmium	6	11.0	10.7	1.3	12.0	±1.19

Notes: **a.** 100(standard deviation/mean)
b. Student's t-test.
c.Combination of the concentration of cadmium already in the soil (0.163 μg g^{-1}) and the added concentration (37.0 μg g^{-1}).

The results given in Table 3·3 indicate acceptable levels of precision (about 10% for cadmium) and a near-zero bias.

Another source of error in the methods described above (section 3·2) is variability in metal concentrations between samples taken from the same site. The results of the analyses of 8 dust samples collected from a 5 m section of Blenheim Road, and 10 samples taken from a 4 m^2 dust patch near Princess Street, are given in Tables 3·4 and 3·5.

Table 3·4

Cadmium, lead and zinc concentrations in eight dust samples taken from a 5 m stretch of Blenheim Road.

Sample number	Concentrations (μg g^{-1})		
	Cadmium	Lead	Zinc
1	0.705	1 600	331
2	1.36	1 510	314
3	1.14	1 570	355
4	0.854	1 610	365
5	1.12	1 790	350
6	0.872	2 030	292
7	0.747	2 060	358
8	1.06	1 980	314
Mean	0.982	1 770	335
Standard deviation	0.225	226	26
Error on mean[a]	±0.165	±166	±19

Note: **a.** Student's t-test, at a 95% confidence level.

Table 3·5

Cadmium, lead and zinc concentrations in ten dust samples taken from a 4 m^2 dust patch.

Sample number	Concentration ($\mu g\ g^{-1}$)		
	Cadmium	Lead	Zinc
1	0.504	275	330
2	0.491	314	345
3	0.639	267	384
4	0.608	459	523
5	0.571	483	544
6	0.609	297	486
7	0.571	446	514
8	0.617	375	459
9	0.635	310	506
10	0.573	289	435
Mean	0.582	352	453
Standard deviation	0.051	83	77
Error on mean[a]	±0.031	±50	±47

Note: a. Student's t-test, at a 95% confidence level.

The mean coefficients of variation (100 x standard deviation/mean) for cadmium, lead and zinc from the data in Tables 3·4 and 3·5 are 15.8%, 18.2% and 12.4%, respectively. These represent real variations over the sample site superimposed upon random analytical variations. In most cases, the concentrations determined for cadmium, lead and zinc in a particular sample differed from the mean values of these metals (determined from all samples) by no more than ±20%. Provided that the data given in Tables 3·4 and 3·5 are true for the general case, the evidence suggests that any particular experimentally determined cadmium, lead or zinc concentration in a single dust sample taken from a reasonably small site is likely to be within ±20% of that metal's "true" concentration at that site (as represented by the mean value). This level of inter-sample variability was seen to be sufficiently low for the purposes of this study.

3·3·2 Cadmium, lead, zinc and organic matter in soil and dust

3·3·2a Background and residential sites

Cadmium, lead and zinc concentrations and the percentage of organic matter in soil and dust from eight "residential" and three "background" locations are given in Tables 3·6 and 3·7.

Table 3·6

Concentrations, mean values, and errors on the mean values of cadmium, lead, zinc and organic matter in residential and background soil samples.

Location		Cadmium concn ($\mu g\ g^{-1}$)	Lead concn ($\mu g\ g^{-1}$)	Zinc concn ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Residential sites					
#1	0-3 cm	0.789	952	607	12.8
	3-6 cm	0.637	870	516	9.72
	6-9 cm	0.655	973	596	8.62
#2	0-3 cm	0.286	64.2	99.3	13.2
	3-6 cm	0.202	77.4	99.8	10.4
	6-9 cm	0.358	70.0	99.8	9.69
#3	0-3 cm	0.448	371	235	13.0
	3-6 cm	0.282	375	218	10.5
	6-9 cm	0.160	366	206	9.73
#4	0-3 cm	0.434	147	302	13.9
#5	0-3 cm	0.316	144	177	17.9
	3-6 cm	0.350	134	179	13.0
	6-9 cm	0.340	118	170	11.4
#6	0-3 cm	0.238	168	104	13.4
	3-6 cm	0.236	158	98.5	9.26
	6-9 cm	0.122	148	87.4	7.23
#7	0-3 cm	0.219	256	180	18.0
#8	0-3 cm	0.166	69.4	87.9	7.47
	3-6 cm	0.171	59.4	81.6	6.15
	6-9 cm	0.114	45.2	81.2	6.10
Mean		0.326	278	211	11.1
Error on mean[a]		±0.074	±119	±67	±1.3
Background sites					
#1	Mean[b]	0.068	34.1	56.8	
	Error on mean[a]	±0.006	±1.4	±7.7	
#2[c]		0.158		48.8	
#3[d]		0.086	52.4	54.0	

Notes: **a.** Student's t-test, at a 95% confidence level.
b. Gebbies' Pass, mean of six analyses of the same sample.
c. Soil from under a house built in *ca.* 1900.
d. Soil from under a house built in 1852.

Table 3·7

Concentrations, mean values, and errors on the mean values of cadmium, lead, zinc and organic matter in dust samples taken from residential areas.

Residential site number	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
1	1.20	1 510	1 090	4.92
2	0.476	348	306	3.93
3	0.622	1 090	326	4.62
4	0.520	1 060	587	15.6
5	1.58	1 250	1 430	11.0
6	0.806	1 300	398	4.96
7	0.525	3 200	1 130	27.7
8	0.463	1 050	1 150	8.41
Mean	0.774	1 350	802	10.1
Error on mean[a] at 95% confidence level	±0.269	±589	±319	5.9

Note: a. Student's t-test.

It can be seen from Table 3·6 that soil from residential areas has about five times more cadmium than soil from Gebbies' Pass, and three times more than the soil from underneath the two old Christchurch houses. This difference is presumably due to the cumulative output of various cadmium sources within Christchurch. Predominant residential sources of cadmium are probably car-tyre wear, the weathering of galvanized-iron roofing and coal combustion (Table 3·1).

In the case of the comparison between cadmium concentrations in residential soils (which are mainly Tai Tapu silt loam) and the mean concentration found in soil from Gebbies' Pass (Rapaki silt loam), some of the difference could be due to dissimilarities in soil composition between the sites (Raeside and Rennie, 1974; Gong *et al.* 1977). This confounding factor is not present in the comparison of residential soil cadmium levels with levels in soil from beneath the two old houses.

Concentrations of cadmium, lead and zinc in soil from residential site 1 are considerably higher than those in soil from the other seven residential areas, suggesting that residential site 1 has experienced a degree of contamination in excess of that which would normally be expected for suburban soils. If the data pertaining to that site are excluded, the residential soil mean concentrations (and their errors at a 95% confidence level) fall to $0.261\pm0.045\ \mu gCd\ g^{-1}$, $147\pm27\ \mu gZn\ g^{-1}$, and $163\pm49\ \mu gPb\ g^{-1}$. Residential soil cadmium concentrations are then seen to be about four times higher than the mean concentration in soil from Gebbies' Pass, and two times higher than the mean concentration in the soil from underneath the old houses.

Suburban soil cadmium concentrations are observed to decrease with depth at residential sites 3 and 6, decrease then increase with depth at sites 1 and 2, and increase then decrease with depth at sites 5 and 8 (Table 3·6). Presumably, the relationship between concentration and depth is dependent to some extent on the history of the sampled site. For example, an increase followed by a decrease in cadmium concentration would be expected if a relatively contaminated soil layer was at some stage covered by a comparatively clean soil layer. Another important factor governing cadmium's depth profile are the effects that redox potential and pH have on its mobility (section 1·3·2). A contaminated soil in Essen, West Germany, was found to have the highest cadmium concentrations at those depths characterized by the highest redox potentials (Hermann and Neumann-Mahlkau, 1985). Thus, differences between the sites in cadmium concentration with depth can be rationalized both on the basis of historical and of physico-chemical considerations. Measurements of variations in redox potential and pH with depth were not made in this study. Officer (1989) reported that the soil pH in 12 Christchurch soil cores remained more or less constant with depth (0–16 cm) within each sample. In addition to this, Christchurch soils are known to be acidic (typical pH values in Officer's study were between pH 5 and 6)—conditions which would favour formation of the (mobile) Cd^{2+} ion. However, the fact that no fixed relationship is apparent between cadmium soil concentrations and depth in residential areas implies that the interpretation of concentration-depth profiles at industrial sites should be undertaken with care (section 3·3·2b). The topic of the pH dependence of cadmium's mobility in a Christchurch soil is addressed in Chapter 11.

3·3·2b Industrial sites

Concentrations of cadmium, lead, zinc and organic matter in soil samples taken from nearby potential sources of cadmium are given in Table 3·8; concentrations in industrial dust samples are given in Table 3·9. In only four cases was there sufficient depth of soil to allow the soil cores to be sectioned according to depth.

Table 3·8

Concentrations of cadmium, lead, zinc, and organic matter in soil from industrial sites. In cases where the depth is unspecified, figures refer to the surface layer (usually 0-4 cm).

Location	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Cement works				
0-3 cm	0.455	92.4	205	
3-6 cm	0.239	77.3	152	
6-9 cm	0.187	46.4	135	
Former Gasworks site	0.282		85.2	
Galvanizing firm	0.873		2 830	

Table 3·8 continued...

Location	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Iron foundry				
0-3 cm	0.360	129	130	
3-6 cm	0.233	94.9	137	
6-9 cm	0.362	241	233	
Plastics factory				
South side				
0-3 cm	0.437	791	143	6.91
3-6 cm	0.316	58.3	117	6.71
6-9 cm	0.294	21.4	119	6.87
North side	0.283	108	195	7.30
Retread factory				
0-3 cm	0.537	100	136	13.9
3-6 cm	0.421	66.8	107	8.79
6-9 cm	0.169	15.0	77.9	5.86
Spray painter	0.880		486	
Steel products manufacturer	0.248	264	172	7.44
Tyre manufacturer				
South side	0.212	128	88.7	11.9
NNE side	0.385	177	885	15.0
East side	0.307	136	85.5	9.21
Tyre retreader	0.397		119	

Table 3·9

Cadmium, lead, zinc and organic concentrations in dust samples from (mainly) industrial sites. Figures in brackets refer to the concentrations in samples taken from the same sites after three weeks of heavy rainfall.

Location	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Aluminium joinery	1.26	1 210	439	2.54
Battery factory	3.55 3.83[a]	302 400	349	6.81
Car wrecker #1	2.30	1 170	736	5.38
#2	20.9	2 340	759	7.05
Cement works	1.42	472	558	
Ceramics factory	1.18	2 380	386	4.14

Table 3·9 continued...

Location	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Electroplating firm #1				
Cd-plating section				
3mwest	200 (20.0)	2 950	42 100 (1 870)	
3m W, 20m S	43.4 36.8[a]	7 900	8 050	
3m W, 40m S	11.7 (14.5)	5 110	49 500 (5 130)	
20m W, 40m S	5.82 (3.40)	1 150	1 280 (811)	
Hard-chroming section				
5m south	19.1 (7.43) 21.8[a]	1 600	2 970 (1 750)	
20m S	2.49 (3.12)	1 040	1 450 (1 050)	
35m E	1.62 (2.21)	688	455 (553)	
50m E	1.15 (1.32)	1 050	985 (950)	
Electroplating firm #2				
70m north	0.820	1 130	1 190	
85m N	1.43	1 370	580	
15m S	1.45	1 820	1 400	
20m S	1.03	1 420	1 230	3.42
35m S	1.73	867	1 070	
100m E	0.641	558	1 210	3.28
70m W	3.28	1 660	2 050	8.08
85m W	0.339	538	426	2.93
Fertilizer works	13.8	1 120	417	10.2
Galvanizing firm	5.39 4.74[a]	1 200	188 000	2.82
Metal merchant #1	1.02	1 460	1 040	7.79
#2	2.00	1 780	3 020	6.83
Metal polishing firm #1	0.836	597	600	5.45
#2	1.35	1 690	763	5.38
#3	0.789	276	357	3.94
#4	2.10	1 620	907	5.50
Metal processing firm #1	2.70	4 190	3 080	4.47
#2	0.961	1 100	3 450	6.05
#3	0.783	1 180	473	4.15
Non-ferrous metal dealer #1	2.10	1 700	1 660	3.45
#2	1.14	1 540	360	
#3	8.85	4 600	2 290	3.97
Plastics factory	0.550		2 370	5.20

Table 3·9 continued...

Location	Cadmium concentration ($\mu g\ g^{-1}$)	Lead concentration ($\mu g\ g^{-1}$)	Zinc concentration ($\mu g\ g^{-1}$)	Organic content (% by weight loss upon ashing)
Retread factory				
under chimney	0.895		708	15.9
20m NE	0.547		456	3.10
40m NE	0.894		813	4.35
60m NE	1.33		520	7.60
76m NE	0.941		534	3.38
Road-dust				
Site #1[b]	1.26	1 280	785	
Site #2	0.852		408	5.35
Scrap-metal merchants #1	1.74	734	390	5.74
#2	1.60	660	557	2.54
#3	2.79	6 200	826	4.86
#4	2.70	3 590	1 130	4.77
Spray painting firm #1	1.58 (0.520)	1 020	812 (504)	7.94 (3.51)
#2	1.01 (2.95)	1 620	863 (2 530)	10.1 (16.1)
#3	1.71 (0.924)	1 790	970 (769)	10.9 (4.45)
#4	7.34 (4.23)	2 940	2 260 (1 030)	5.58
#5	1.51 (3.40)	1 400	548 (1 190)	4.06 (5.44)
Tyre manufacturing firm	1.03	1 660	480	6.96
Tyre vulcanizing firm	1.87 (2.55)	1 910	1 020 (1 280)	5.40
Welding firm #1				
outside	1.27	1 730	938	3.38
20m E	0.797	836	517	1.86
40m E	0.783	1 380	563	3.09
80m E	1.01	1 930	991	3.51
150m E	1.44	4 080	680	3.14
10m W	1.22	3 350	1 650	
20m W	1.03	1 920	624	
70m W	2.04	1 950	360	
Welding firm #2	80.0 (4.82)		6 300 (811)	
#3	2.60 (1.66)		1 030 (749)	
#4	4.67 (3.64)		2 700 (5 650)	
#5	2.57 (10.7)		1 940 (2 010)	
Zinc coating firm	1.18	931	447	

Notes: **a.** Sample collected on 11 February 1988.
b. Mean of ten samples from Lyttleton.

The absolute concentrations of cadmium in soils from industrial sites (Table 3·8) are not particularly high. In non-polluted agricultural soils the cadmium concentration can range from 0.01 to 0.7 $\mu g\ g^{-1}$ (Piotrowski and Coleman, 1980). This can be compared with the

the highest soil cadmium concentration found in this study; 0.880 $\mu g\ g^{-1}$. Overseas, soils in well-established industrialized regions can contain considerably more cadmium, an example being soil from the Heisinger Aue area of the Ruhr district, West Germany, where cadmium levels were found to have reached 30 $\mu g\ g^{-1}$ (Hermann and Neumann-Mahlkau, 1985). It is apparent then, that the industries listed in Table 3·8 which are sources of cadmium (identified below) are not emitting enough cadmium, and/or have not been operational for a long enough time to cause accumulations of the metal in soils of similar magnitudes to those seen overseas.

Soils from nearby the cement works, plastics factory and retread factory show generally decreasing concentrations of cadmium with depth. However, because the same trend was observed for two of the residential soils (section 3·3·2a) the concentration-depth profile was thought to be an insufficient basis for point-source classification in Christchurch.

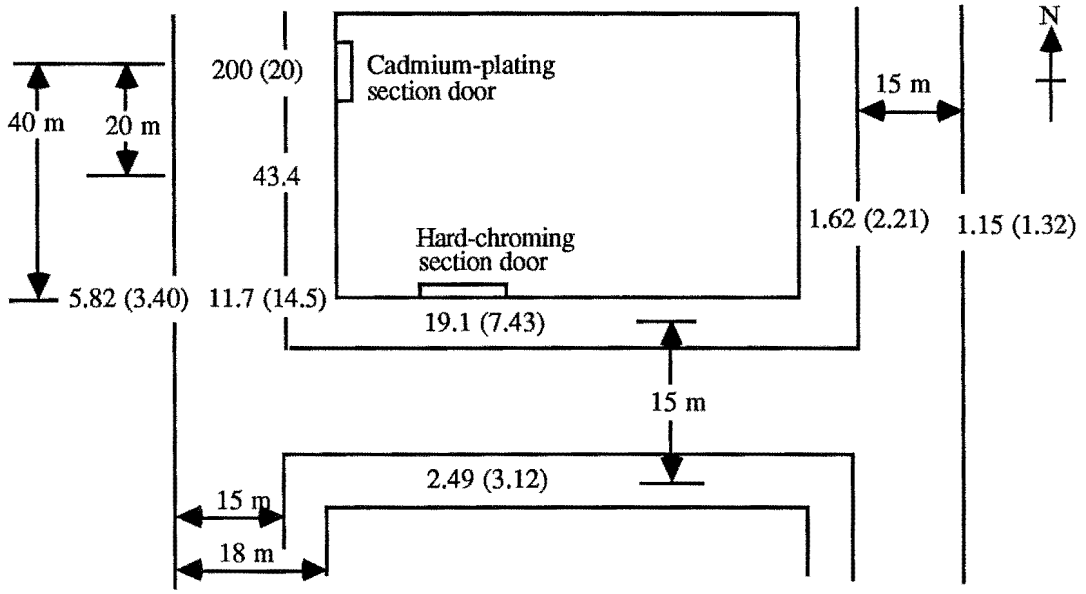
From Table 3·9, the following observations and deductions can be made:

1. The concentrations of cadmium in industrial dust ranged from 0.339 $\mu g\ g^{-1}$ in dust from 85 m west of one electroplating firm to 200 $\mu g\ g^{-1}$ in dust from 3 m west of another electroplating firm. There is a much larger range of cadmium, lead and zinc concentrations in dust than in soil samples. This probably reflects a greater variety of sources of these three metals in the dust.
2. In activities such as welding and spray-painting, the emission of cadmium varies from one firm to another. This is consistent with expectations, as the use of cadmium alloys by welders, or cadmium sulphide and thioselenide paints by spray-painters would be intermittent (Table 1·1).
3. Again corresponding with cadmium's intermittent use, the concentrations of cadmium in samples collected after three weeks of heavy rainfall are sometimes higher and sometimes lower than the concentrations in samples taken from the same sites after four rainless weeks. However, the mean value of the factor obtained by dividing pre-rainfall cadmium concentrations by their post-rainfall counterparts is 2.67 ($n = 17$), with a standard deviation of 4.24. The Student's t-test 95% confidence interval on this mean stretches from 0.82 to 4.53. Because this interval excludes zero, it can be stated that overall, rainfall caused a significant reduction in the cadmium levels in the dust samples. The same thing can be said for zinc, for which the mean reduction factor upon rainfall (in the same samples) is 3.29 (standard deviation 5.58) and the 95% confidence interval is 0.85-6.58. Fergusson and Simmonds (1983) also observed a fall in zinc and cadmium concentrations in Christchurch road-dust after a period of heavy rainfall.
4. Natural and man-made obstructions, coupled with the general "one-sidedness" of most of the industries, made it difficult to assess the effect of wind direction on cadmium concentrations. For this type of study a tall cadmium-emitting chimney would be ideal. In the two cases examined which involved tall chimneys, no discernible trends involving dust cadmium concentrations were evident.

5. Cadmium concentrations diminish with increasing distance from the source, and this is exemplified by the data concerning the first electroplating firm, which is presented pictorially in Figure 3·1.

Figure 3·1

Dust cadmium concentrations (in $\mu g\ g^{-1}$) in the vicinity of electroplating firm #1. Figures in brackets refer to the concentrations after three weeks of heavy rainfall.



It can be calculated from the data in Table 3·9 that the mean reduction in cadmium concentration with distance from the electroplating firm is 1.35 $\mu gCd\ g^{-1}\ m^{-1}$. The actual reduction along any given stretch would be highly dependent on such factors as wind direction and local geographic features (such as walls). However, in general terms the cadmium concentrations are seen to decrease rather rapidly with increasing distance from the firm, so that 85 m east of the source (at the roadside) measured concentrations are only 1.6 times higher than the residential mean value for roadside dust (Table 3·7). Most of the contamination, then, appears to be limited to the immediate environment of the electroplating firm. If this data can be taken to be true for the general case, it would be expected that cadmium liberated from each point-source would have a negligible influence on residential cadmium levels. The fact that residential soil cadmium concentrations are about 2-4 times higher than concentrations in background soil would then imply that widely-dispersed and frequently encountered sources are operational in residential areas. This scenario is consistent with the idea that widespread entry into the suburban environment of relatively small amounts of cadmium occurs *via* such sources as the weathering of unpainted galvanized-iron surfaces, car tyre wear and coal combustion. The effect of galvanized-iron roofing on the cadmium and zinc concentrations of house-dust is

examined in Chapter 4. Cadmium concentrations in rubber from car tyres are examined in Chapter 5, and those in aerosols in Chapter 7.

6. In the four cases where a second sample was collected approximately one year after the first, concentrations of cadmium are almost identical between the two samplings. Apparent changes in the dust cadmium concentration after one year were +7.9% (battery factory), –15.2% (electroplating firm 3 mW, 40 mS), +14% (electroplating firm, 5 mS of hard chroming section), and –12.1% (galvanizing firm). Thus, the mean percentage change after one year was only –1.4% (standard deviation 14%). This result suggests that although the levels of cadmium in the dusts are high, cadmium is not accumulating in them, but has reached a "steady-state" concentration. This would require that inputs of cadmium to the dusts from the industrial processes were matched by outputs. Outputs could involve the dispersal of contaminated dust by wind, the effect of rainfall, and the dilution of contaminated dust by incoming (cadmium-low) dusts.

Sources of cadmium can be identified by comparison of the cadmium concentrations found in soil and dust collected near them (Tables 3·8 and 3·9) with the mean cadmium concentrations in residential soil or dust (Tables 3·6 and 3·7). The "Enrichment Factor [Residential]" will be taken to represent the ratio obtained by dividing the metal concentration in the dust or soil at a particular site by the residential mean dust or soil concentration of that metal. The use of the residential mean—rather than the background mean—cadmium concentration as the denominator is necessary in order to distinguish point-sources of cadmium from probable city-wide sources, such as car tyre wear (Table 3·1). Enrichment Factors [Residential] of cadmium, lead and zinc in soil and dust collected from near those sites regarded as potential sources of cadmium are given in Table 3·10. For the reasons already given (section 3·3·2a), data relating to residential site 1 have been omitted from the calculation of the mean cadmium, lead and zinc levels in residential soil.

Table 3·10

Enrichment Factors [Residential] of cadmium, lead and zinc in industrial soil and dust samples, for use in source identification. Figures in brackets refer to the Enrichment Factors [Residential] in dust samples taken after three weeks of heavy rainfall.

Location	Enrichment Factors [Residential]		
	Cadmium	Lead	Zinc
Soil samples			
Cement works	1.13	0.441	1.12
Former Gasworks site	1.08		0.580
Galvanizing firm	3.34		19.3
Iron foundry	1.22		1.13

Table 3·10 continued...

Location	Enrichment Factors [Residential]		
	Cadmium	Lead	Zinc
Plastics factory			
south side	1.34	1.78	0.859
north side	1.08	0.663	1.33
Retread factory	1.44	0.372	0.728
Spray painter	3.37		3.31
Steel products maker	0.950	1.61	1.17
Tyre manufacturer			
south side	0.812	0.785	0.603
NNE side	1.48	1.09	6.02
east side	1.18	0.834	0.582
Tyre retreader	1.52		0.810
Dust samples			
Aluminium joinery	1.63	0.894	0.547
Battery factory	4.76[a]	224	0.435
Car wrecker#1	2.99	0.866	0.918
#2	27.0	1.73	0.946
Cement works	1.83	0.350	0.696
Ceramics factory	1.52	1.76	0.481
Electroplater #1[b]	44.4 (9.59)	1.99[c]	16.6[c] (2.16)
#2[d]	1.91	0.866	1.43
Fertilizer works	17.8	0.833	0.520
Galvanizing firm	6.54[a]	0.887	234
Metal merchant#1	1.32	1.08	1.30
#2	2.58	1.31	3.76
Metal polisher#1	1.08	0.442	0.748
#2	1.74	1.25	0.951
#3	1.02	0.204	0.445
#4	2.71	1.20	1.13
Metal processor#1	3.49	3.10	3.84
#2	1.24	0.815	4.30
#3	1.01	0.874	0.590
Non-ferrous			
metal dealer#1	2.71	1.26	2.07
#2	1.47	1.14	0.449
#3	11.4	3.41	2.86
Plastics factory	0.710		2.96
Retread factory[d]	1.19		0.756
Road-dust			
site 1[b]	1.63		0.978
site 2	1.10		0.509
Scrap-metal			
merchants #1	2.25	0.554	0.486
#2	2.07	0.489	0.695
#3	3.60	4.59	1.03
#4	3.49	2.66	1.41
Spray-			
painting firms #1	2.04 (0.672)	0.756	1.01 (0.628)
#2	1.30 (3.81)	1.20	1.08 (3.15)
#3	2.21 (1.19)	1.33	1.21 (0.959)
#4	9.48 (5.47)	2.18	2.82 (1.28)
#5	1.95 (4.39)	1.04	0.683 (1.48)
Tyre manufacturing firm	1.33	1.23	0.599
Tyre vulcanizing firm	2.42 (3.29)	1.41	1.27 (1.60)

Table 3·10 continued...

Location	Enrichment Factors [Residential]		
	Cadmium	Lead	Zinc
Welding firms #1[e]	1.55	1.59	0.986 (1.01)
#2	103 (6.23)		7.86 (0.934)
#3	3.36 (2.14)		1.28 (7.04)
#4	6.03 (4.70)		3.37 (2.51)
#5	3.32 (13.8)		2.41
Zinc coating firm	1.52	0.690	0.557

Notes: **a.** Calculated from the mean of 2 samples.
b. Calculated from the mean of 10 samples.
c. Calculated from the mean of 8 samples.
d. Calculated from the mean of 5 samples.
e. Calculated from the mean of 7 samples.

If sources of cadmium are defined as those activities which give rise to cadmium concentrations of above twice the appropriate residential mean value, a cut-off point which seems reasonable considering the errors involved (section 3·3·1), the following can be classified as sources: one battery factory and fertilizer works; one (each) electroplating, galvanizing, metal merchant, metal polishing, metal processing, and tyre vulcanizing firm; two car wrecking and metal-dealing firms; four scrap-metal merchant and welding firms; and five spray-painting firms. Thus, a total of 13 different activities (at 25 locations) have been identified as point-sources of cadmium in Christchurch. In the cases of 10 of the 13 point-sources identified, the cadmium was (presumably) not used intentionally, but was in some way associated with the activity taking place. In the remaining three cases (welding, spray-painting and electroplating) cadmium and/or its compounds were (presumably) being used intentionally (section 1·2·1). (It should also be mentioned that the fact that a particular activity has not been identified in this survey as a source of cadmium does not rule out its being one, as the use of cadmium products can be intermittent, as in the case of spray-painting.)

The intrinsic toxic potential of the street dust near sources of cadmium can also be estimated. This area concerns young children more than it does adults, both because their behavioural patterns (such as frequent sucking of the hands) ensure that they get a regular intake of road-dust, and because they are generally more susceptible to a given dosage of toxic material than are adults (Duggan and Williams, 1977; Fergusson and Schroeder, 1985). In this study the mean residential cadmium concentration in dust was found to be 0.774 $\mu g\ g^{-1}$ (Table 3·7). It has been estimated that, on average, pre-school children will ingest between 10 and 100 mg of road-dust per day (Duggan and Williams, 1977). For those activities identified as sources of cadmium (above) a mean dust cadmium concentration of about 8 $\mu g\ g^{-1}$ can be calculated. From these figures it follows that the average daily road-dust derived cadmium intake of pre-school children living in residential areas is likely

fall in the region of 0.008 to 0.08 μg, whereas the road-dust derived intake of children living near a source of cadmium is (on average) likely to be 10 times higher: 0.08–0.8 μg. Of this, an estimated 25% might be absorbed across the gut (Fergusson, 1990). Thus, a pre-school child living near a source of cadmium might be expected to absorb 0.02–0.2 μgCd day^{-1} from road-dust. This figure represents less than 1% of the amount of cadmium normally absorbed by young children from food sources (Muskett *et al.* 1977 and Chapter 15). In other words, the intake and absorption of cadmium by young children living near point-sources of cadmium from road-dust is likely to be relatively small.

3·3·3 Correlations and speciations of cadmium in soil and dust

3·3·3a Correlations

Data concerning the extent of cadmium's correlations with lead, zinc and organic matter in soil and dust samples are presented in Table 3·11. Because the data sets were positively skewed (and approximately log-normal), values were transformed to their natural logarithms prior to the derivation of correlation coefficients.

Table 3·11

Correlations between cadmium and lead, cadmium and zinc, and cadmium and organic matter in Christchurch soil and dust.

Correlated pair	Number of pairs	Correlation coefficient (r)	Probability[a]	Significance of correlation	Least squares relationship
Soil					
ln[Cd], ln[Zn]	41	0.655	<0.001	Highly	ln[Zn]=0.857ln[Cd]+6.13
ln[Cd], ln[Pb]	42	0.596	<0.001	Highly	ln[Pb]=0.986ln[Cd]+6.13
ln[Cd], ln%Org.	31	0.388	<0.05	Just	ln%Org.=0.292ln[Cd]+2.67
Dust					
ln[Cd], ln[Zn]	94	0.611	<0.001	Highly	ln[Zn]=0.563ln[Cd]+6.60
ln[Cd], ln[Pb]	62	0.319	<0.02	Quite	ln[Pb]=0.369ln[Cd]+7.04
ln[Cd], ln%Org.	57	0.111	>0.1	Not	

Note: a. According to Pearson's tables.

Strong linear relationships exist between the concentrations of cadmium and zinc, and cadmium and lead, in both dust and soil samples. Geochemically, cadmium is associated with zinc and lead (section 1·2·1). When either of these metals is employed in an industrial process, the possibility exists that cadmium will be released. The results of this study show that cadmium levels in Christchurch soil and dust have a high degree of association with zinc and lead levels, suggesting that at many of the sites sampled, cadmium was not liberated alone, but in association with lead and/or zinc. Closer examination of Table 3·10 confirms this suspicion. If sources of lead and zinc are defined in the same way as sources of cadmium—those activities which give rise to nearby dust lead and zinc

concentrations of above twice the appropriate residential mean values—the following facts become apparent:

1. Nine sources of cadmium are also sources of zinc (four welding and two spray-painting firms, one (each) electroplating firm, galvanizing firm and non-ferrous metal dealership).
2. Three sources of cadmium are also sources of lead (one battery factory and two scrap-metal merchants).
3. Three sources of cadmium are also sources of both lead and zinc (one metal processing firm, spray-painting firm and non-ferrous metal dealership).
4. The remaining ten cadmium sources are not sources either of lead or of zinc (three spray-painting firms, two scrap-metal merchants and car wrecking firms, one tyre vulcanizing and metal-polishing firm, and one fertilizer works).

Thus, 15 out of the 25 sources of cadmium identified in this survey are also sources of lead and/or zinc.

In the samples studied, soil cadmium concentrations are mildly correlated ($p<0.05$) with the amount of organic matter in the soil (Table 3·11). (There is no evidence of such a relationship in the case of dust samples.) A correlation between the cadmium concentration and organic content of various soils has previously been noted by a number of workers (Gerritze and Van Driel, 1984; Haas and Horowitz, 1986; Petruzzelli *et al.* 1978; Pickering, 1980; Ram and Verloo, 1985). The adsorption capacity of a soil for a metal is dependent on the strengths of the metal-ion interactions with the soil's components, the three most significant components in terms of adsorptivity being the clay, organic and hydrous metal oxide fractions (Laxen, 1983; Garcia-Miragaya and Page, 1978; section 1·3·2). The relative adsorptivities of the various components of a Christchurch soil are examined in Chapter 10.

3·3·3b Magnetic fractionation

The relative weights of the magnetic and non-magnetic fractions of five samples, and the concentrations and total amounts of cadmium in them are given in Table 3·12.

A mean recovery of 82% (standard deviation 15%) can be calculated from the data in Table 3·12 by comparison of the calculated total concentrations after fractionation with the concentrations measured prior to fractionation. In terms of cadmium concentrations ($\mu g\ g^{-1}$) in magnetic and non-magnetic fractions, no clear pattern is evident. Two samples have substantially higher concentrations in the magnetic fraction, two have higher concentrations in the non-magnetic fraction, and in the remaining sample cadmium concentrations are split more or less evenly between both fractions. However, in terms of the total amount of cadmium (μg), in all five cases the greatest proportion is found in the non-magnetic fraction, due to the greater contribution of this fraction to the overall weight of the samples.

Table 3·12

Concentrations and amounts of cadmium in, and weights of, magnetic and non-magnetic fractions of five dust samples.

	Car wrecking firm #2	Electroplating firm #1	Electroplating firm #1	Spray painting firm #4	Welding firm #2
Weight (g)					
magnetic	0.770	1.09	0.680	2.06	2.11
non-magnetic	5.81	9.49	4.11	12.3	2.94
% of total weight					
magnetic	11.7	10.3	14.2	14.4	41.8
non-magnetic	88.3	89.7	85.8	85.6	58.2
Concentration of cadmium[a] ($\mu g\ g^{-1}$)					
magnetic	43.0	22.1	33.3	10.1	27.0
non-magnetic	11.7	223	13.7	2.86	66.6
Amount (μg) of cadmium[b]					
magnetic	33.1	24.1	22.6	20.8	57.0
non-magnetic	68.0	2120	92.9	35.1	196
% of total cadmium[c]					
magnetic	32.7	1.1	19.6	37.2	22.5
non-magnetic	67.3	98.9	80.4	62.8	77.5
Calculated[c] total [Cd] after fractionation ($\mu g\ g^{-1}$)	15.4	202	16.5	3.90	50.0

Notes: **a.** Total concentrations before fractionation are given in Table 3·9.
b. Weight x concentration.
c. Totals here taken as μgCd[magnetic] x weight[magnetic] + μgCd[non-magnetic] x weight[non-magnetic].

The degree to which cadmium associates with the magnetic fraction would depend on the type of cadmium compound used (Table 1·1) and the ability of that compound to react with—or adsorb onto the surface of—materials containing the ferromagnetic elements iron, nickel and cobalt. Both parameters would vary depending on the industrial process. Some cadmium alloys are made which contain nickel (Hollander and Parker, 1978). Reactivity itself would be markedly influenced by phase changes. Adsorption, for instance, would be more likely when the cadmium compound is released as a vapour, as it would be during cadmium-alloy soldering operations.

The magnetic and non-magnetic fractions of the two dust samples with the highest levels of cadmium (the 200 $\mu g\ g^{-1}$ sample from near an electroplating firm and the 80 $\mu g\ g^{-1}$ sample from near a welding firm) were analysed using an electron microprobe (technique described in Chapter 14). Although this technique allows the qualitative and quantitative analysis of portions of a sample as small as 1 μm^2, the minimum concentration

of cadmium required to be present in such an area for reliable detection is about 500–1 000 μg g^{-1} (Flaws, 1988). Because the highest cadmium level in the dust samples was 223 μg g^{-1}, electron microprobe analysis was expected to detect cadmium only if it was heterogeneously distributed through the samples, as it would be if the sample contained small fragments of metallic cadmium. No such cadmium concentrations were detected by electron microprobe analysis in any of the four samples.

The negative results obtained using the electron microprobe technique imply that either cadmium was homogeneously distributed through the dust, or it was heterogeneously distributed through the dust but at low concentrations. This leads to the speculation that emissions of cadmium from the welding and electroplating firms were likely to have been in the form of vapours, rather than of small fragments (>1 μm) of cadmium metal. The significance of this is that cadmium vapour is potentially more damaging to human health than other forms of cadmium emissions (section 1·4).

Metallic looking fragments separated from the non-magnetic fraction of the dust sample taken from near the welding firm were also analysed by XRPD (technique described in Chapter 14). To be detected by XRPD, the analyte must usually comprise greater than 5% of the sample (Fergusson, 1988). The range of d-spacings (Å) and their relative intensities (subscripts) obtained over the two-theta angular range 20–100° were 2.34_{10}, 2.03_4, 1.43_2, 1.22_2 and 1.17_1 ; corresponding in all cases with those of aluminium. Once again, no cadmium was detected.

3·3·3c Size–density relationships

The weights of, and concentrations (μg g^{-1}) and amounts (μg) of cadmium in, four size fractions of 11 dust samples are given in Appendix 3·2. Concentrations and amounts of cadmium in, and weights of, five density fractions of eight dust samples are given in Appendix 3·3. Percentage weights and percentage of total amounts of cadmium in the size and density fractions are given in Appendices 3·4 and 3·5. Graphs of the size-density relationships for the eight dust samples where both parameters were measured are presented in Figures 3·2 (concentrations) and 3·3 (total μg) (pages 56–59).

In terms of concentrations (μg g^{-1}) of cadmium, the following conclusions can be drawn from the data in Appendices 3·2–3·5 and Figure 3·2.

1. Concentrations are generally highest in the two smallest size fractions (<149 μm). A general trend of increasing cadmium concentration with decreasing size is observed. This phenomenon is well documented for trace metals in sediments (Horowitz, 1985) and has been observed to occur in Christchurch road dust in the case of lead by Fergusson *et al.* (1980) and in the cases of 18 elements (including cadmium and lead) by Fergusson and Ryan (1984). It is thought to occur primarily because the surface area/weight ratio increases markedly with decreasing particle size, effectively presenting more sites for surface–metal interactions (such as adsorption) to take place. (For example, very coarse sand has a surface area/weight ratio of 11.3 cm^2 g^{-1}, whereas the figure for fine clay is about 45 000 cm^2 g^{-1} (Horowitz, 1985).)

Figure 3·2

Concentrations of cadmium (μg g^{-1}) in various size and density fractions of eight dust samples

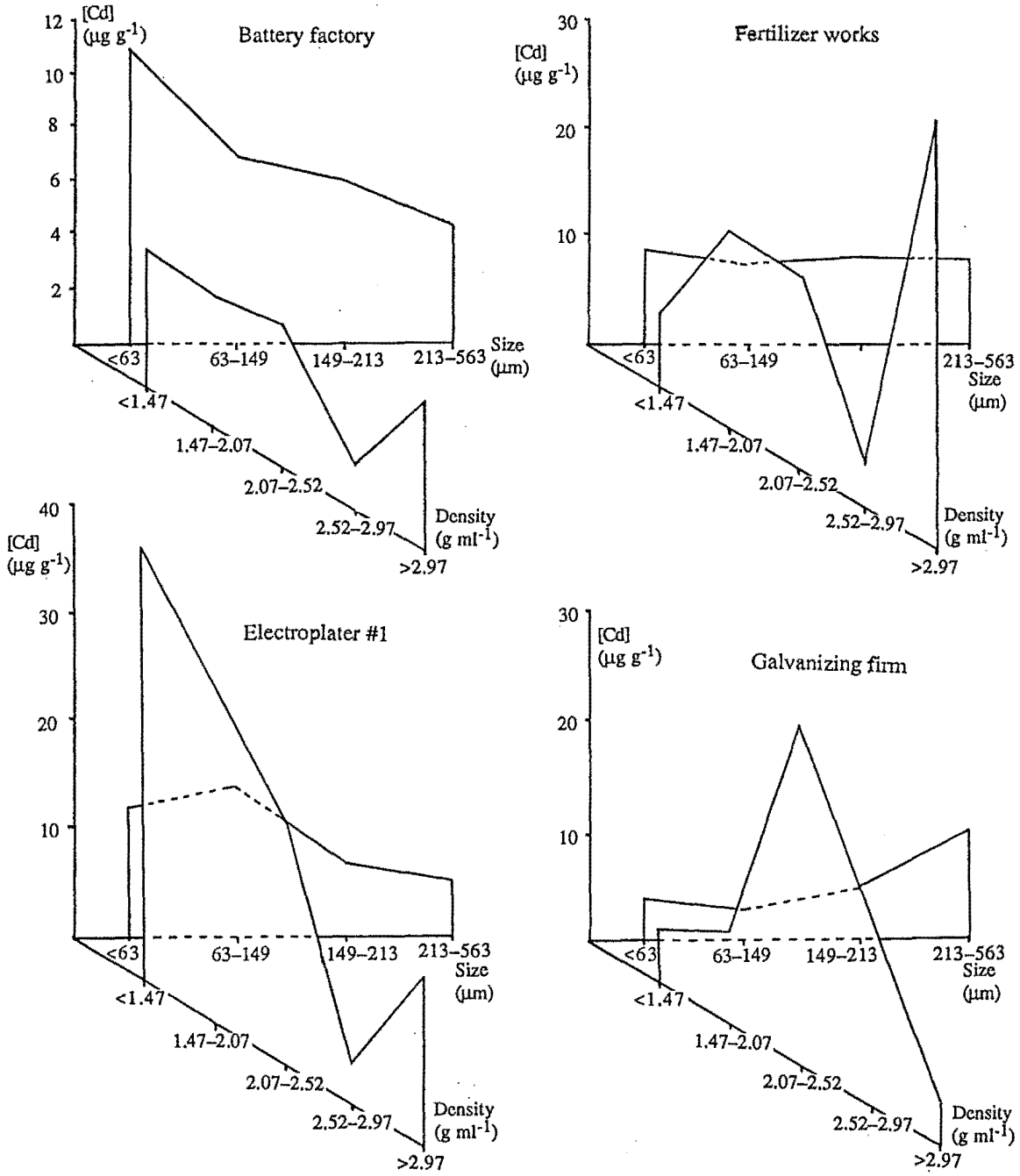


Figure 3·2 continued...

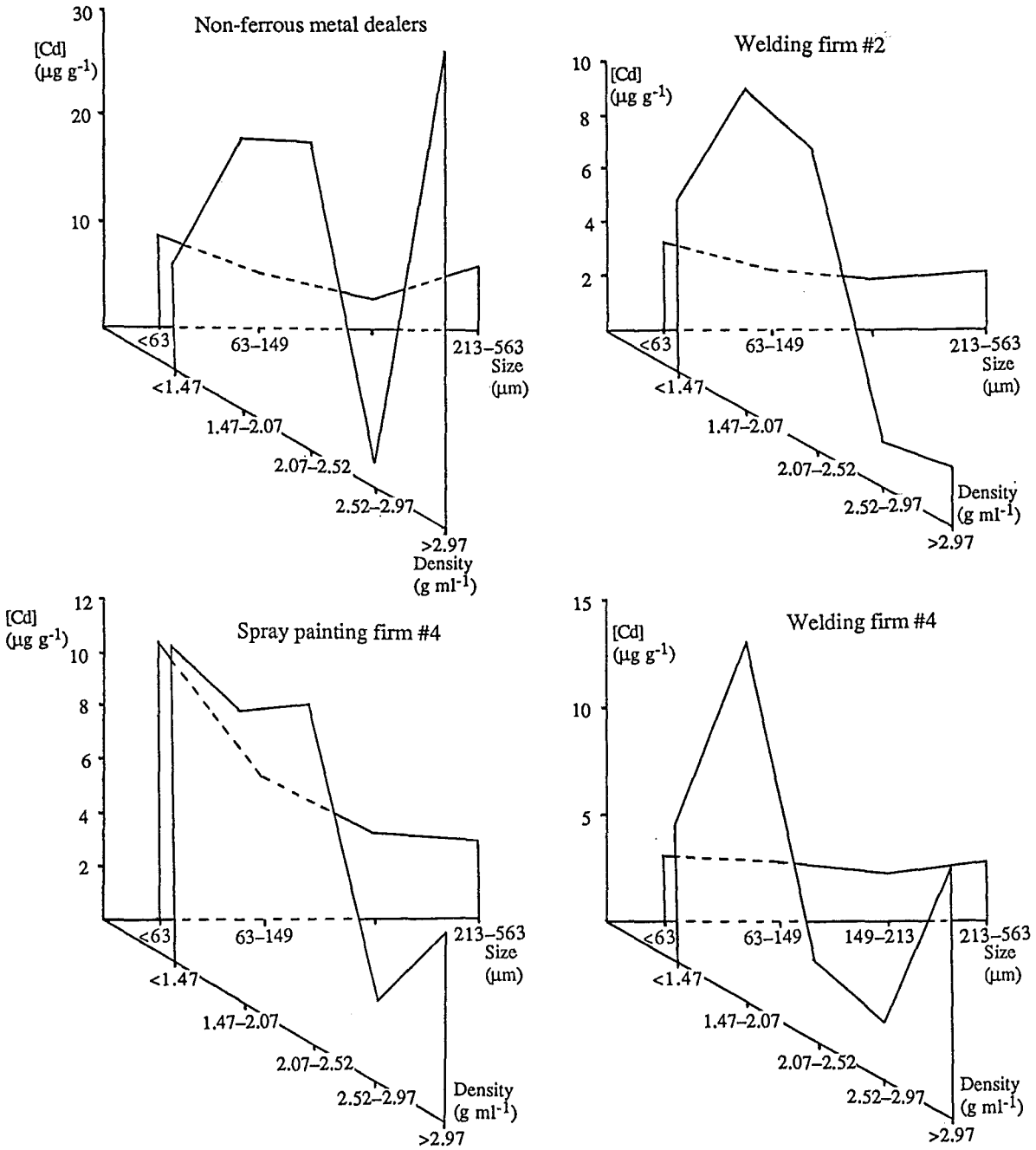


Figure 3·3

Total amounts of cadmium (µg) in various size and density fractions of eight dust samples

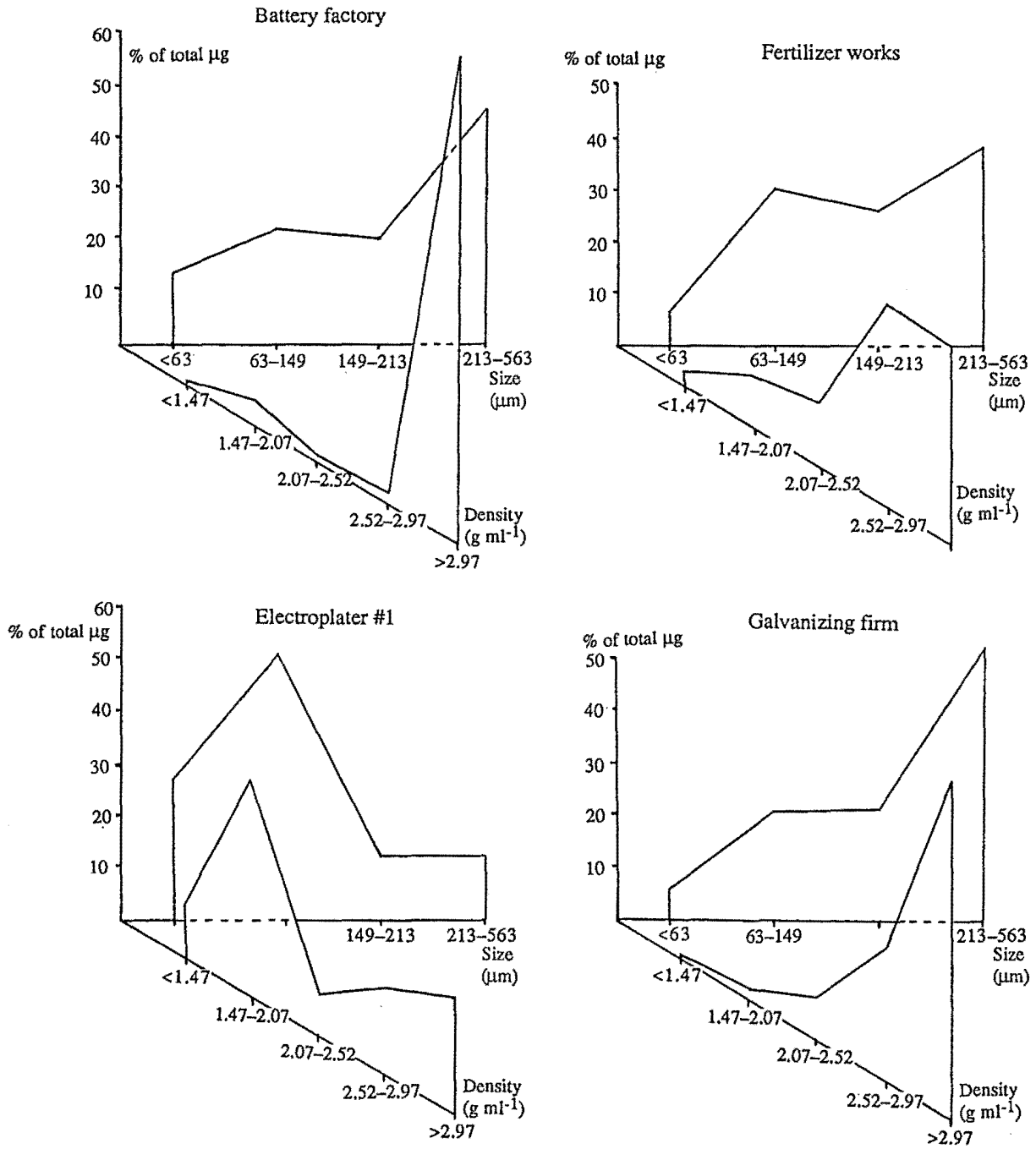
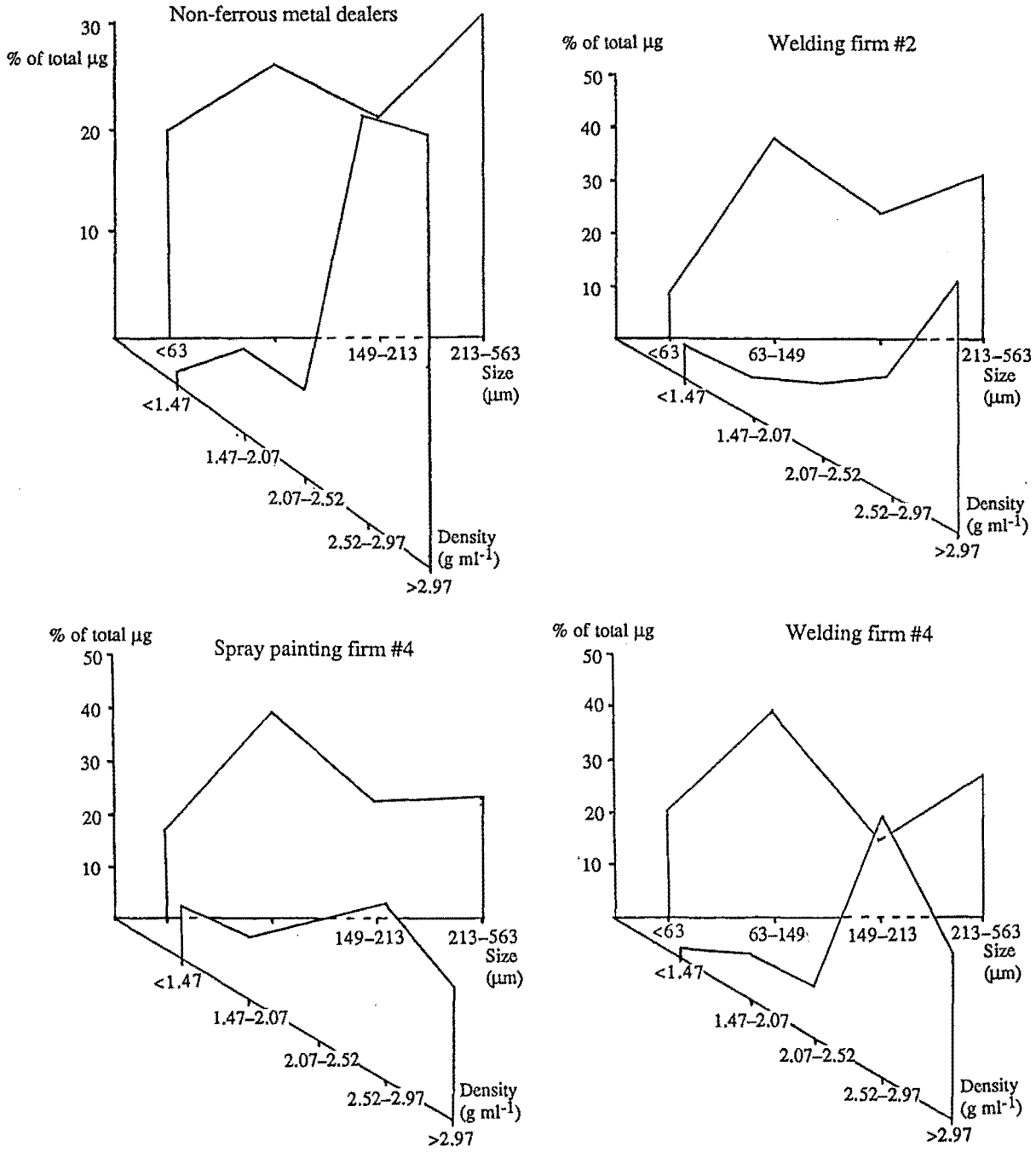


Figure 3·3 continued...



If cadmium fumes were released during an industrial process, adsorption onto the surface of dust particles could take place directly from the gas phase. Adsorption could also occur during rainfall, *via* solubilization of Cd^{2+}. A reversal of the above trend is evident in dust from near the galvanizing firm, in which the highest concentrations of cadmium are associated with the coarsest size fraction (213–563 μm). A possible reason for this could be that the cadmium in this sample is mainly associated with zinc, which itself makes up about 20% of the sample (by weight). Johnson *et al.* (1982) found that whereas most of the cadmium in house-dust was located in the finer fractions, zinc was consistently concentrated in the coarsest fractions.

2. Except in the case of the galvanizer, concentrations of cadmium are always lowest in the density fraction 2.52–2.97 g ml^{-1}. This is probably caused by quartz sand (SiO_2, density 2.64–2.66 g ml^{-1}) acting as a diluent, as it is likely to be relatively cadmium-free (Chapter 10) (Weast and Astle, 1983). The two most dense fractions in all samples also represented most of the total weight.
3. The highest concentrations of cadmium are found in the most dense (>2.97 g ml^{-1}) fraction in three cases, in the mid-density (2.07–2.52 g ml^{-1}) fraction in three cases, and in the least dense (<1.47 g ml^{-1}) fraction in the case of the electroplater. Explanations for these observations would depend on the densities of the different cadmium species (and the particles they were associated with) in the dusts, and on the extent to which cadmium-low diluent species are present within each fraction. The large concentrations of cadmium in the high density (>2.97 g ml^{-1}) fraction of the dust from near the non-ferrous metal dealer could represent cadmium metal (density 8.64 g ml^{-1}) or cadmium associated with other metallic species. Correlations have already been noted to occur in the dust between concentrations of cadmium and those of both lead and zinc (section 3·3·3a). The similar trend in cadmium concentration with density in the case of the fertilizer works, however, is probably a result of cadmium incorporated into the (relatively high density) phosphate rocks and phosphatic-fertilizers handled by the company (section 2·1·2e).(The sample itself appeared to contain a large proportion of such material.) The enhanced concentrations of cadmium in the mid-to-low density fractions of the dust sample collected from near a spray-painting firm may reflect an association of cadmium sulphide and thioselenides with organic solvents of low-to-mid density in the paint. Conversely, the similar trends observed in the cases of the two welding firms and the electroplating firm may result from cadmium being liberated as a vapour and then becoming adsorbed onto the surface of fine (and predominantly low density) dust particles. Thus, the different industrial operations can apparently give rise both to similar and to dissimilar cadmium concentration–density profiles for different reasons.

Changes upon (mathematical) transformation from concentrations (μg g^{-1}) to amounts (μg) of cadmium in each fraction are dominated by three factors. Firstly, in almost

all (9 of the 11) samples, the smallest size fraction (<63 μm) has the least total weight. Correspondingly, in 9 of the 11 size-fractionated samples, the amount of cadmium (μg) is the smallest in the finest size fraction, even though this fraction generally contains the highest concentrations of cadmium (Figure 3·3). Secondly, the highest proportions of the total weight are represented by the coarsest (213–563 μm) size fraction in six cases, and by the 149–63 μm fraction in the remaining five cases. Accordingly, in a given sample, the amount of cadmium (μg) is always the highest in one of these two fractions. Thirdly, in all eight cases the two fractions of density exceeding 2.52 g ml^{-1} represent most of their sample's total weight; the result of which is that in seven of the eight density-fractionated samples, the amount of cadmium is greatest in the two most dense fractions. Thus, in the samples studied, the total amount of cadmium in a given size or density fraction was generally controlled more by the total weight of that fraction than by the concentration of cadmium therein.

It can be assumed that lead particles (density 11.3 g ml^{-1}) in the 302 000 μgPb g^{-1} battery factory dust sample, and fragments of zinc (density 7.14 g ml^{-1}) in the 188 000 μgZn g^{-1} galvanizing firm dust sample would both settle in the highest density fraction (>2.97 g ml^{-1}). Dust particles heavily adsorbed with lead or zinc might also be expected to sink in this fraction. The observation that 90% of the total weight of each of these two dust samples was located in the most dense fraction tends to confirm this. In the sample from near the galvanizing firm, the concentration of cadmium in the high-density fraction is the lowest of all fractions (the cadmium content of the zinc is apparently low), whereas in the battery factory dust sample, the concentrations of cadmium are more or less equal in all five density fractions. However, once again, because the high density fraction of both samples accounts for most of the total weight, most of the cadmium is found there; 64% in the galvanizing firm dust sample, and 93% in the battery factory dust sample (Appendices 3·3 and 3·5).

3·3·3d Other speciations

Four residential soil and eight industrial dust samples were sequentially extracted, using the method of Tessier *et al.* (1979). The results of the sequential extraction study are given in Chapter 12.

3·4 Conclusion

A variety of anthropogenic point-sources of cadmium operational within Christchurch have been identified on the basis of a comparison of the cadmium concentrations found in dust from nearby them with those found in residential dust and soil samples. These sources, predominantly industrial in nature, include both processes where cadmium was used intentionally (spray painting, electroplating, and welding) and operations where cadmium is more "inadvertently" involved (battery factory, fertilizer works, galvanizing firm, retread

factory, and a variety of metal-processing operations). Fifteen of the 25 sources of cadmium identified in this survey are also sources of lead and/or zinc.

The concentrations of cadmium in the industrial soil samples are comparatively low; in industrial dusts they are higher, but still unlikely to constitute a direct risk to public health. The highest dust cadmium level observed was 200 $\mu g\ g^{-1}$ in a sample collected from outside an electroplating company. Concentrations of cadmium diminished rapidly with increasing distance from this firm, and it seems likely that the effect of industrial sources on suburban cadmium levels is negligible. Rainfall caused a significant reduction in dust cadmium concentrations. However, there is some evidence to suggest that levels at any particular industrial site remain more or less constant with time, having reached a "steady state" where inputs of cadmium from the industrial process are matched by outputs.

Cadmium is correlated with zinc and lead both in soil and in dust samples, and with organic matter in soil samples. The results of electron microprobe analysis suggest that cadmium may be homogeneously distributed through the dusts. Cadmium concentrations generally increase with decreasing particle size, suggesting adsorption of cadmium onto the dust has occurred. (This could take place either during the industrial process or after it.) Concentration–density relationships are more variable, but can often be rationalized on the basis of the industrial process involved.

3·5 References

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3·6 Appendices

Appendix 3·2 (section 3·3·3)

Weights, total amounts of cadmium, and cadmium concentrations in the four size fractions of 11 dust samples.

	Weight (g)				Cd concn (μg g^{-1})				Amount of Cd (μg)[a]			
Size (μm)	563–213	213–149	149–63	<63	563–213	213–149	149–63	<63	563–213	213–149	149–63	<63
Battery factory	4.56	1.46	1.42	0.520	4.36	6.03	6.86	10.8	19.9	8.80	9.74	5.62
Electro-plater 1												
5mW 40mS	3.37	2.56	5.16	3.22	5.03	6.76	13.8	11.8	17.0	17.3	71.2	38.0
5m S	2.96	1.78	1.98	0.548	5.53	3.66	6.15	8.44	16.4	6.51	12.2	4.64
3m W	1.39	0.871	1.43	0.592	6.88	11.0	14.0	13.5	9.56	9.57	20.0	7.97
Fertilizer works	2.81	1.92	2.39	0.450	7.77	7.99	7.25	8.17	21.8	15.3	17.3	3.68
Galvanizing firm	3.31	2.92	4.85	1.06	9.58	4.45	2.63	3.50	31.7	13.0	12.8	3.71
Non-ferrous metal dealer	1.03	1.52	0.989	0.419	5.55	2.65	5.03	8.40	5.72	4.03	4.98	3.53
Spray-painter #4	0.981	0.882	0.960	0.200	2.96	3.25	5.26	10.2	2.90	2.86	5.05	2.04
Tyre vulcanizer	3.68	2.46	2.82	0.930	1.23	1.58	1.89	2.54	4.53	3.89	5.33	2.36
Welder #2	3.19	2.80	3.75	0.530	2.08	1.92	2.21	3.20	6.64	5.38	8.29	1.70
Welder #4	2.22	1.48	3.18	1.60	2.75	2.09	2.81	2.90	6.11	3.09	8.94	4.64

Note: a. Weight x concentration.

Appendix 3·3 (section 3·3·3)

Weights, total amounts of cadmium, and cadmium concentrations in the five density fractions of eight samples.

	Battery factory	Electro-plater #1	Fertilizer works	Galvan-izing firm	Non-Fe metal dealer	Spray painter # 4	Welder #2	Welder # 4
Weight (g)								
< 1.47 g ml^{-1}	0.040	0.325	0.326	0.194	0.060	0.404	0.604	0.146
1.47–2.07 g ml^{-1}	0.846	1.72	0.338	0.219	0.159	0.547	0.334	0.269
2.07–2.52 g ml^{-1}	0.128	0.500	0.411	0.250	0.142	0.932	0.731	1.36
2.52–2.97 g ml^{-1}	1.40	5.97	5.42	1.33	7.70	5.71	7.58	10.3

Appendix 3·3 continued...

	Battery factory	Electro-plater #1	Fertilizer works	Galvan-izing firm	Non-Fe metal dealer	Spray painter # 4	Welder #2	Welder # 4
> 2.97 g ml^{-1}	18.0	1.89	0.607	19.5	0.505	1.84	11.7	1.65
Concentration of cadmium (µg g^{-1})								
<1.47 g ml^{-1}	5.01	39.8	6.85	4.57	9.36	11.7	6.08	6.34
1.47–2.07 g ml^{-1}	4.89	29.7	18.0	7.99	25.2	10.8	12.0	16.8
2.07–2.52 g ml^{-1}	5.17	22.6	17.9	30.8	28.5	12.7	11.3	3.75
2.52–2.97 g ml^{-1}	1.77	3.61	4.60	18.3	2.58	3.07	1.81	2.78
>2.97 g ml^{-1}	5.54	15.3	40.7	3.18	44.5	7.40	2.34	11.9
Amount of cadmium[a] (µg)								
<1.47 g ml^{-1}	0.200	13.0	2.23	0.890	0.563	4.72	3.68	0.926
1.47–2.07 g ml^{-1}	4.14	51.5	6.08	1.75	4.01	5.91	4.01	4.53
2.07–2.52 g ml^{-1}	0.662	11.3	7.36	7.71	4.04	11.8	8.25	5.09
2.52–2.97 g ml^{-1}	2.49	21.6	24.9	24.2	19.9	17.5	13.7	28.7
>2.97 g ml^{-1}	99.5	28.9	24.7	62.0	22.5	13.6	27.3	19.6

Note: **a.** Weight x concentration.

Appendix 3·4 (section 3·3·3)

Percentage of total weights, and of total amounts of cadmium in four size fractions of 11 dust samples.

	Percentage of total weight				Percentage of total µg cadmium			
	563–213	213–149	149–63	<63 µm	563–213	213–149	149–63	<63 µm
Battery factory	57	18	18	7	45	20	22	13
Electroplater #1								
5m W 40m S	23	18	36	23	12	12	50	26
5m S	41	25	27	7	41	16	31	12
3m W	33	20	33	14	20	20	42	18
Fertilizer works	37	25	32	6	38	26	30	6
Galvanizing firm	27	24	40	9	52	21	21	6
Non-Fe metal dealer	26	38	25	11	32	22	27	19
Spray-painter #4	33	29	32	6	23	22	39	16
Tyre vulcanizing firm	37	25	29	9	28	24	33	15
Welder #2	31	27	37	5	30	24	38	8
Welder #4	26	18	38	19	27	14	39	20

Appendix 3·5 (section 3.3.3)

Percentage of total weights, and of total amounts of cadmium in five denstity fractions of eight dust samples.

	Battery factory	Electro-plater #1	Fertilizer works	Galvan-izing firm	Non-Fe metal dealer	Spray painter # 4	Welder #2	Welder # 4
Percentage of total weight								
< 1.47 g ml^{-1}	0.2	3	5	1	1	4	3	1
1.47–2.07 g ml^{-1}	4	17	5	1	2	6	2	2
2.07–2.52 g ml^{-1}	0.6	5	6	1	2	10	3	10
2.52–2.97 g ml^{-1}	7	57	76	6	90	60	36	75
>2.97 g ml^{-1}	88	18	8	91	5	20	56	12
Percentage of total amount of cadmium								
< 1.47 g ml^{-1}	0.2	10	3	1	1	9	6	2
1.47–2.07 g ml^{-1}	4	41	9	2	8	11	7	8
2.07–2.52 g ml^{-1}	0.6	9	12	8	8	22	14	9
2.52–2.97 g ml^{-1}	2	17	38	25	39	33	24	49
>2.97 g ml^{-1}	93	23	38	64	44	25	48	32

CHAPTER 4
CADMIUM, COPPER, LEAD AND ZINC IN CHRISTCHURCH HOUSE-DUST: CONCENTRATIONS AND SOURCES

4·1 Introduction

There is an increasing awareness of the potential contribution that house-dust can make to the levels of trace metals in humans. Young children have been identified as the highest risk group for two reasons. Firstly, young children are more likely to ingest significant quantities of dust than adults; and secondly, young children are usually more susceptible to a given intake of toxin than adults (Duggan and Williams, 1977). "Pica" (the mouthing of non-food objects), and repetitive hand or finger sucking are thought to be the two main dust ingestion routes (more or less) unique to children (Brunekreef, 1983; Sturges and Harrison, 1985).

The potential for a trace metal found in house-dust to have an effect on a child's body burden of that metal has been well illustrated in the case of lead. Several researchers have concluded, for example, that a quantitative relationship exists between household dust lead levels and blood lead levels in children (Charney, 1980; Sayre, 1981; Angle *et al.*, 1983; Brunekreef, 1983; Duggan, 1983). It has also been shown that, for children, the quantity of lead ingested from various dusts by the hand-to-mouth route can often equal or exceed that ingested through the diet (Duggan, 1983; Thornton, 1985).

Studies examining the cadmium concentrations of house-dusts have been undertaken less frequently than studies relating to lead. Solomon and Hartford (1976) reported cadmium concentrations as high as 105 $\mu g\ g^{-1}$ in house-dusts from a small urban community in Illinois, U.S.A. Muskett *et al.* (1979) sampled house-dust from 40 homes in London and the Home Counties (U.K.) and calculated the mean cadmium concentration of the dusts to be 24 $\mu g\ g^{-1}$ (range 0.05–63 $\mu g\ g^{-1}$). More recently, Thornton *et al.* (1985) conducted a study in the United Kingdom involving 5 228 houses (in 53 towns and villages) and found the house-dust geometric mean cadmium concentration to be 6.8 $\mu g\ g^{-1}$.

In all studies where the subject has been examined, higher concentrations of lead and cadmium have been found in house-dust than in garden soil. Thornton *et al.* (1985) calculated that on average, six times more cadmium and two times more lead was in the internal house-dust of the properties sampled than was in their garden soil. Because ingestion of dust by a child is more likely to occur within the house, it follows that house-dusts constitute a greater potential health-risk than do external dusts (Harper and Sullivan, 1987).

The aims of this section of the thesis were both to obtain reliable data describing the concentrations ($\mu g\ g^{-1}$) and amounts ($\mu g\ m^{-2}$) of cadmium in house-dusts from residential areas of Christchurch, and to identify factors which influence the concentrations and amounts of cadmium in Christchurch house-dusts. As a result of this second aim, the

concentrations and amounts of copper, lead and zinc were also determined, as these are the three metals with which cadmium is associated geochemically (section 1·2·1). This work also complements earlier studies carried out in Christchurch by Fergusson *et al.* (1985, 1986) relating to the lead concentrations and elemental composition of house-dusts.

Throughout this Chapter, the term *concentration* will be taken to represent $\mu gM\ g^{-1}$, and the term *amount* will be taken to refer to $\mu gM\ m^{-2}$, where M is the metal concerned.

4·2 Method

4·2·1 Sample selection and collection

Eight residential suburbs of Christchurch were chosen for this study. Fifteen houses were selected at random from each of these suburbs (total sample size 120 houses) by the following procedure. A calculator-generated random number (0–1) was multiplied by the number of pages in the "Christchurch City" section of the Christchurch Telephone Directory, resulting in the creation of a random page number. The appropriate page was scanned (top to bottom, left to right) until an address in the target suburb was located; people living at the address were telephoned and an appointment was arranged. The suspicion level was relatively high, and the appointment-to-telephone-call ratio was about 0.2. After each appointment was made, another page was randomly selected.

The suburbs selected were St. Albans, Sydenham, Linwood, Upper Riccarton, Wainoni, Bryndwr, St. Martins/Huntsbury and Hoon Hay; corresponding with the eight principal compass directions relative to the central city of N, S, E, W, NE, NW, SE and SW. The positions of the houses surveyed are given in Appendix 3·1 (inside back cover).

It was felt that the houses sampled represented a fairly wide socioeconomic cross-section of what was available. However, in terms of people there tended to be a slight bias toward retired persons and single-income families with children. This was simply because representatives of these two groups tended to spend more time at home, and were therefore more likely both to be at home when the initial telephone-call was made, and to be available at a later date for sampling to proceed. Considering that the group to whom trace metals in house-dusts pose the greatest potential health-threat is children, the slight bias toward houses where children are most often found may be advantageous.

Three samples were collected from different sections of the carpet in the living-area (lounge) of each house. Sampling was undertaken during September and October 1987, using the method introduced by Solomon and Hartford (1976). Dust was collected by suction onto a Gelman Type A glass-fibre filter of 37 mm diameter. Suction was provided by a small electric vacuum pump, capable of producing a vacuum of 27 kPa. The filter was held in a Gelman three-piece plastic field monitor, which was moved slowly and systematically across the carpet until an area of 0.25 m^2 had been covered.

During sampling, the three-piece plastic holder held the glass-fibre filter about 6 mm from the carpet. Each sample was stored in a clean plastic bag. Prior to sampling,

the filters were brought to constant humidity over dried silica gel and then weighed; after sampling, the process was repeated.

At the time of sampling, information was collected concerning house age, material, roof type, and paint colour; carpet wear, colour, and rubber underlay existence; fireplace existence; the number of doors and square metres of opening windows to the room being sampled; traffic density; and the occupations of the residents. The carpet use and traffic density measurements were semi-qualitative (estimated); the former being on a 0 (new) to 3 (threadbare) scale, and the latter on a scale of 0 (*cul de sac*) to 5 (main road). Appendix 4·1 is a list of the variables used and how their categories were classified.

4·2·2 Analysis of samples and quality control

Samples (filters with dust on them) were digested in 4 M AR nitric acid (15 ml) for 30 minutes. Each solution was then filtered (through a nitric acid and double-distilled water washed Whatman No. 540 filter paper); the residue was washed with double-distilled water until the filtrate reached a volume of 25 ml. Cadmium concentrations in the extracts were determined by GFAAS, using the furnace heating program (and other parameters) given in section 3·2·2. Solution copper, lead and zinc concentrations were determined by FAAS, using the parameters given in Chapter 14. Background correction was used in all cases. Standards were prepared from 1 000 $\mu g\ ml^{-1}$ stock solutions, and made up to the same acid strength as the samples (2.4 M). Clean glass fibre filters were digested for use as sample blanks.

Analytical precision and bias were estimated by repeated analysis of a previously well characterized internal-reference street-dust sample (Fergusson, 1987), the results for which were seen to be acceptable and are given in Table 4·1.

Table 4·1

Comparison of assumed concentrations of cadmium, copper, lead and zinc in an internal-reference street-dust sample with concentrations determined in this study.

	Cadmium	Copper	Lead	Zinc
Assumed concentration ($\mu g\ g^{-1}$)	1.30	204	10 800	455
This study:				
Number of analyses	8	8	8	8
Mean concentration ($\mu g\ g^{-1}$)	1.17	209	10 700	424
Standard deviation ($\mu g\ g^{-1}$)	0.12	16	800	33
Coefficient of variation[a] (%)	10	8	8	8

Note: **a.** 100[standard deviation/mean].

The efficiency of the extraction method was assessed by performing a second nitric acid extraction on 12 house-dust samples, and using GFAAS to analyse the resulting

solutions (parameters given in Chapter 14). It was found that the first extraction had removed 99.5% of the cadmium, 98.3% of the copper, 99.3% of the lead, and 98.9% of the zinc (standard deviations 0.59%, 0.87%, 0.46% and 1.05%, respectively).

The method of standard additions indicated that for all four metals, no significant interferences (>4%) were present in the sample solutions.

4·3 Results and discussion

4·3·1 Summary statistics

The full set of data obtained in this survey is given in Appendix 4·2. A breakdown of the data by suburb is presented in Appendix 4·3. Statistics summarizing the full set of data are given in Table 4·2, and the results of this study are listed alongside the results of other studies in Table 4·3.

Table 4·2

Summary statistics relating to the dustiness (mg m^{-2}) and the concentrations (μg g^{-1}) and amounts (μg m^{-2}) of cadmium, copper, lead and zinc in Christchurch house-dust. Total sample size (n) = 120 mean values[a].

	Dustiness	Concentrations (μg g^{-1})				Amounts (μg m^{-2})			
	(mg m^{-2})	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Geometric mean	181	4.24	165	573	10 400	0.75	28.3	98.9	1 700
Arithmetic mean	404	5.15	190	724	21 700	1.81	69.4	324	1 870
Standard deviation	683	3.50	127	577	35 400	3.23	132	650	879
Error on mean[a] at 95% confidence level	±122	±0.63	±23	±103	±6 330	±0.58	±24	±116	±157
Range: lower	7.15	0.557	54.2	101	871	0.038	1.41	4.55	309
upper	5 680	21.0	1 010	3 510	205 000	26.5	972	4 040	7 300
Median	198	4.23	165	573	8 980	0.684	23.5	85.8	1 690

Notes: **a.** Means of the three samples taken at each house.
b. Normal distribution.

Coefficients of variation relating to the three samples taken from each house were calculated. The mean coefficients of variation (each representing n = 120 values) of the dustiness (mg m^{-2}) and the amounts (μg m^{-2}) of cadmium, copper, lead and zinc are 26.3%, 33.2%, 28.0%, 29.4% and 12.9%, respectively. The mean coefficients of variation of the concentrations (μg g^{-1}) of cadmium, copper, lead and zinc are 28.3%, 19.1%, 19.2% and 29.5%, respectively. These coefficients provide a measure of the mean degree of variability in the dustiness, metal concentrations and metal amounts between the three samples taken from each house.

Table 4·3

Comparison of the results of this study with those of other studies.

Location	Year	Concentrations ($\mu g\ g^{-1}$) Cadmium	Copper	Lead	Zinc
Christchurch					
House-dust					
Arithmetic mean	1981[a]			615	
	1984[b]			672	
	1987[c]	5.15	190	724	21 700
Geometric mean	1987[c]	4.24	165	573	10 400
Soil					
Arithmetic mean	1987[d]	0.326	17.5	278	211
United Kingdom[e]					
House-dust					
Geometric mean	1985	6.8	204	507	1 055
Soil					
Geometric mean	1985	1.2	53	230	260

Notes: **a.** Fergusson and Schroeder, 1985.
b. Fergusson *et al.* 1986.
c. This survey.
d. Chapter 3 this work and Fergusson *et al.* 1986 for copper.
e. Thornton *et al.* 1985.

The following conclusions can be drawn from the data in Tables 4·2 and 4·3 and Appendix 4·3.

1. The geometric mean cadmium concentration of the 120 houses sampled is 4.24 $\mu g\ g^{-1}$ and the range is 0.557 to 21.0 $\mu g\ g^{-1}$. The (geometric) mean lead concentration is 573 $\mu g\ g^{-1}$ (range 101–3 510 $\mu g\ g^{-1}$). Geometric mean (or median) metal concentrations and amounts probably represent "typical" concentrations and amounts more accurately than arithmetic means, as most of the data sets are positively skewed. This being the case, the true 95% errors on the arithmetic means are likely to be higher than those given in Table 4·2, which are (of necessity) based on the assumption that the data is normally distributed. An estimate of a child's average daily intake of cadmium and lead (the two metals which are toxic and cumulative) from house-dust can be made in the same manner as in section 3·3·2b. It has been estimated that the "average" 2-year old is likely to ingest between 10 and 100 mg of house-dust per day (Duggan and Williams, 1977). About 40% of the lead and 25% of the cadmium orally administered will be absorbed by a child's gut (Duggan and Williams, 1977; Fergusson, 1990; Förstner, 1980). Ingestion of cadmium and lead by a 2-year old from food sources are reported to be approximately 10 $\mu gCd\ 24hr^{-1}$ and 75 $\mu gPb\ 24hr^{-1}$ (Friberg *et al.* 1974; Duggan and Williams, 1977). By calculation, and with recourse to the mean cadmium concentration found in this survey (Table 4·2) it follows that a 2-year old might be expected to absorb about

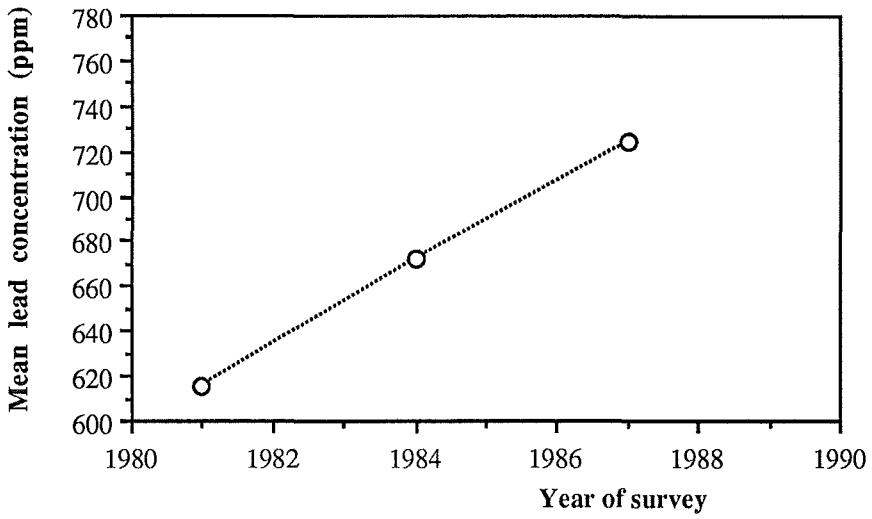
0.01–0.11 μgCd $24hr^{-1}$ from house-dust—which corresponds to 0.4–4% of the amount typically absorbed from food. These figures would not usually be considered to be very significant. For a child living in the home with the highest measured cadmium concentration (21.0 μg g^{-1}), the cadmium absorbed from house-dust could be equivalent to about 20% of that absorbed from food. In terms of lead, a 2-year old might be expected to absorb an *average* of 15%, and a maximum value (in this survey) of 94%, as much lead from house-dust as from his or her food. In contrast to the situation with cadmium, these figures are significant. In the worst scenario, the quantity of lead absorbed by a young child from house-dust could equal the amount absorbed from food. On a moderating note, the actual proportion of houses with house-dust lead concentrations at the higher end of the range is apparently lower in Christchurch than in the United Kingdom. Thornton *et al.* (1985) calculated that 10% of the houses surveyed in Britain had house-dust lead concentrations exceeding 2 000 μg g^{-1} . In this survey, the figure is 6%.

2. Considering geographical differences, the mean concentrations of cadmium, copper and lead in house-dusts appear to be remarkably similar between Christchurch (New Zealand) and the United Kingdom. This tends to suggest that these three metals have similar sources and/or follow similar enrichment patterns in the two countries. The fact that zinc concentrations are about 10 times higher in Christchurch than in the United Kingdom implies that Christchurch has a significant additional source of zinc. This could be galvanized-iron roofing, uncommon in the British Isles but frequently used in New Zealand. The reason why cadmium is not similarly enriched (*i.e.*in Christchurch house-dust compared with house-dust from Britain) could be that high-purity zinc is used in galvanizing. Three samples of galvanized-iron roofing material were analysed and found to contain a mean zinc concentration of 54 000 μg g^{-1} (standard deviation 2 600 μg g^{-1}), but a mean cadmium concentration of only 0.225 μg g^{-1} (standard deviation 0.019 μg g^{-1}). Assuming that the cadmium was entirely associated with the zinc (and not with the iron) the cadmium content of the zinc in the galvanized-iron samples analysed was therefore only 0.0004%. This can be compared with the natural abundance of cadmium in the zinc mineral sphalerite: 0.1–0.5% (Förstner, 1980). Differences between countries in the cadmium and zinc content of rubber underlays and carpet backings could also have an effect—this subject is examined in section 4·3·3c.
3. The (arithmetic) mean concentration of lead in Christchurch house-dust determined in this study compares well with figures reported in earlier studies undertaken in Christchurch (Table 4·3). The apparent increases in (arithmetic) mean lead concentrations between studies are not statistically significant (insofar as the 95% confidence levels for the mean concentrations of lead between studies overlap). The increases could represent a continuing accumulation of lead in Christchurch homes with time, or they could simply reflect methodological dissimilarities between surveys. However it should be noted that the three mean points represent a straight

line—the correlation coefficient between years and mean house-dust lead concentrations is unity (Figure 4·1).

Figure 4·1

Changes in (arithmetic) mean lead concentrations in Christchurch house-dust with time.



The equation of the line is $\mu gPb\ g^{-1} = 598 + 18.2$ (year – 1980), and the F-test probability is 0.017. Thus, although the individual differences between means are not statistically significant, a linear regression between the means and the years they were measured is. Nevertheless, in view of the low number of data points, it is felt that further sampling would be necessary to determine (unambiguously) whether or not the lead concentration in Christchurch house-dusts is increasing with time.

3. Relative to the concentrations found in residential soils, all four metals studied are enriched in the house-dust. This result is in agreement with the results of other studies, and it has been assumed that the phenomenon is caused by the selective (relative) enrichment of the finer (heavy metal rich) dust particles. The selective importation of small particles (on footwear or as aerosols), and the preferential removal of the coarser fractions during cleaning have been suggested as two mechanisms by which this might occur (Sayre and Katzel, 1979; Thornton *et al.* 1985). Enrichment factors in the house-dust relative to residential soil mean values (section 3·3·2a) are in the order zinc (103) > cadmium (15.8) > copper (10.9) > lead (2.60). The extremely high enrichment factor for zinc suggests that significant indoor sources of the metal are operative—one of these sources could be the rubber of carpet underlays or backings. Johnson *et al.* (1982) showed that the character of particles is altered within the household (with respect to the character of external dusts) and suggested that the introduction of matrix components unique to the indoor environment could be one reason for this.
4. From Appendix 4·3 it can be seen that differences in cadmium, copper, lead and zinc concentrations between suburbs are not statistically significant.

4·3·2 Relationships between the metals

The frequency distributions of most data sets were skewed, and found to be approximately log-normal. Each value was therefore transformed to its natural logarithm prior to the derivation of the correlation matrix. The correlation matrix is given in Appendix 4·4. Data concerning the most significant correlations and their least-squares relationships are given in Table 4·4. As an aid to the visualization of dust–metal and metal–metal relationships, a dendogram constructed from the correlation matrix is given in Figure 4·2.

Table 4·4

The most significant correlations present between cadmium, copper, lead, zinc and overall dustiness in Christchurch house-dust and their degrees of significance. Least-squares equations are given in cases where the correlation is highly significant. (Number of data pairs = 120).

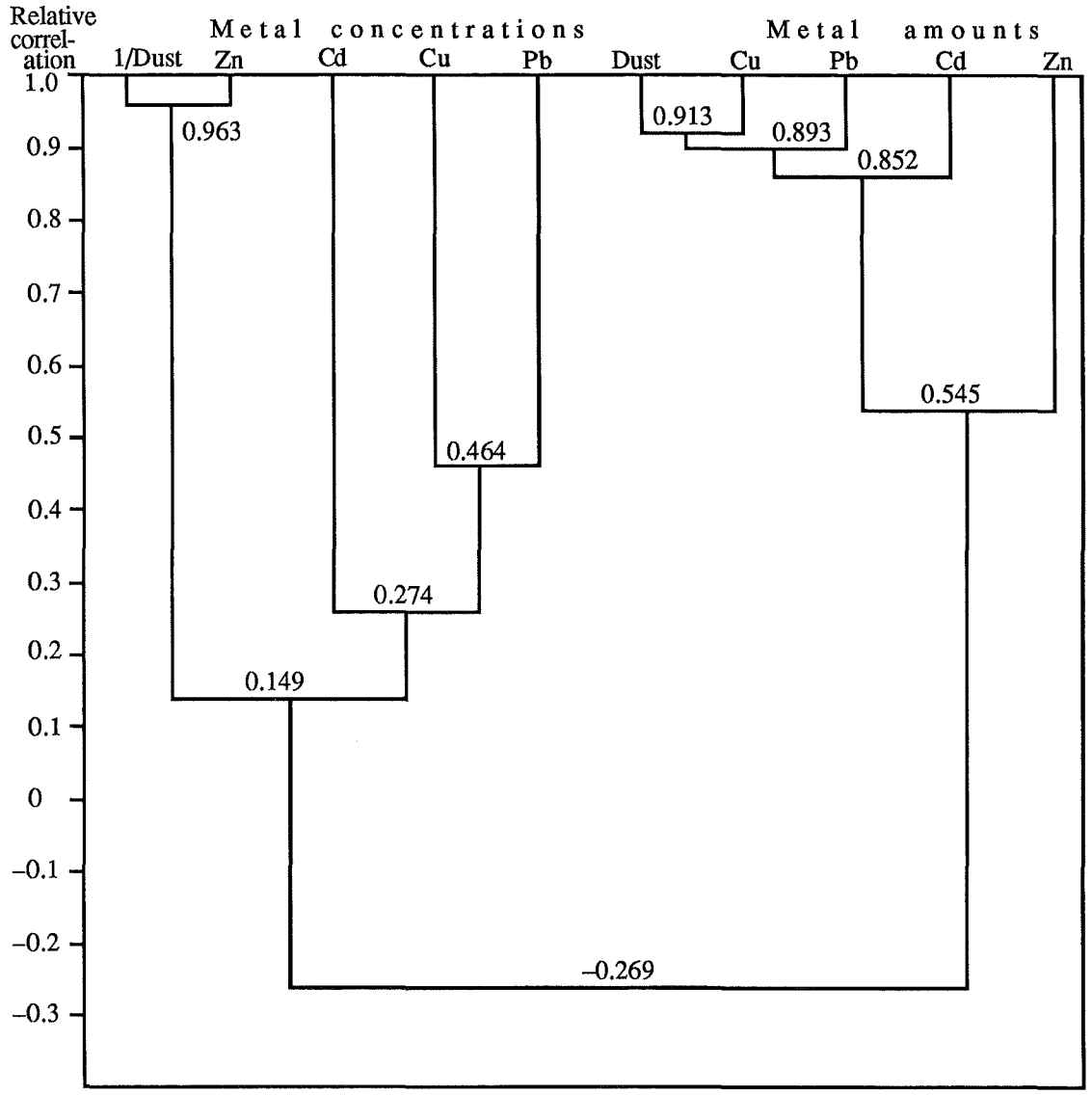
Correlated pair[a]	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
mgDust m^{-2} with...				
$\mu gCd\ m^{-2}$	0.891	<0.001	Highly	$\ln[\mu gCd\ m^{-2}]=0.912\ln[mgDust\ m^{-2}]-5.03$
$\mu gCu\ m^{-2}$	0.913	<0.001	Highly	$\ln[\mu gCu\ m^{-2}]=0.915\ln[mgDust\ m^{-2}]-1.42$
$\mu gPb\ m^{-2}$	0.873	<0.001	Highly	$\ln[\mu gPb\ m^{-2}]=1.01\ln[mgDust\ m^{-2}]-0.661$
$\mu gZn\ m^{-2}$	0.423	<0.001	Highly	$\ln[\mu gZn\ m^{-2}]=0.140\ln[mgDust\ m^{-2}]+6.71$
$\mu gZn\ g^{-1}$	–0.973	<0.001	Highly	$\ln[\mu gZn\ g^{-1}]=0.841\ln[1/mgDust\ m^{-2}]+13.7$
$\mu gCd\ m^{-2}$, $\mu gCu\ m^{-2}$	0.855	<0.001	Highly	$\ln[\mu gCd\ m^{-2}]=0.874\ln[\mu gCu\ m^{-2}]-3.21$
$\mu gCd\ m^{-2}$, $\mu gPb\ m^{-2}$	0.830	<0.001	Highly	$\ln[\mu gCd\ m^{-2}]=0.734\ln[\mu gPb\ m^{-2}]-3.66$
$\mu gCd\ m^{-2}$, $\mu gZn\ m^{-2}$	0.447	<0.001	Highly	$\ln[\mu gCd\ m^{-2}]=1.38\ln[\mu gZn\ m^{-2}]-10.6$
$\mu gCu\ m^{-2}$, $\mu gPb\ m^{-2}$	0.912	<0.001	Highly	$\ln[\mu gCu\ m^{-2}]=0.790\ln[\mu gPb\ m^{-2}]-0.286$
$\mu gCu\ m^{-2}$, $\mu gZn\ m^{-2}$	0.543	<0.001	Highly	$\ln[\mu gCu\ m^{-2}]=1.64\ln[\mu gZn\ m^{-2}]-8.89$
$\mu gPb\ m^{-2}$, $\mu gZn\ m^{-2}$	0.527	<0.001	Highly	$\ln[\mu gPb\ m^{-2}]=1.84\ln[\mu gZn\ m^{-2}]-9.10$
$\mu gCu\ g^{-1}$, $\mu gPb\ g^{-1}$	0.464	<0.001	Highly	$\ln[\mu gCu\ g^{-1}]=0.343\ln[\mu gPb\ g^{-1}]+2.93$
$\mu gCd\ g^{-1}$, $\mu gCu\ g^{-1}$	0.294	<0.01	Very	
$\mu gCd\ g^{-1}$, $\mu gPb\ g^{-1}$	0.254	<0.01	Very	
$\mu gCd\ g^{-1}$, $\mu gZn\ g^{-1}$	0.267	<0.01	Very	
$\mu gCu\ g^{-1}$, $\mu gZn\ g^{-1}$	0.210	<0.05	Just	
$\mu gPb\ g^{-1}$, $\mu gPb\ m^{-2}$	0.510	<0.001	Highly	$\ln[\mu gPb\ g^{-1}]=0.228\ln[\mu gPb\ m^{-2}]+5.30$

Note: a. Correlations are between the natural logarithms of the values of the listed variables.

The amounts (in $\mu g\ m^{-2}$) of cadmium, copper, lead and zinc are related to each other through the level of dust ($mg\ m^{-2}$). Amounts of all four metals show "highly significant" correlations with the level of dust; consequently, the amount of each metal is highly correlated with the amounts of the other three. It is likely that intercorrelations of metal amounts caused by dustiness are superimposed upon pre-existing metal–metal intercorrelations. This theory is supported by the fact that the relative rankings of the correlation coefficients (Figure 4·2) are the same for the amounts of metals as they are for the metal concentrations.

Figure 4·2

Dendogram constructed from the correlation matrix (Appendix 4.4) showing dust–metal and metal–metal inter-relationships. (In the original data the dustiness was in units of mg m^{-2}, metal concentrations were in μg g^{-1}, and amounts were in μg m^{-2}; correlations relate to the natural logarithms of the values of each variable.)



The single greatest correlation between metal concentrations (μg g^{-1}) is that of copper with lead (0.464). This may indicate that the two metals share the same dominant source. Cadmium concentrations show "very significant" ($p<0.01$) to "highly significant" ($p<0.001$) relationships with the other three metal concentrations, the strongest one being (surprisingly) not with zinc, but with copper (0.294). Similarly, copper shows positive correlations with the other three metals. Lead and zinc are the only pair of metals that in terms of concentrations are uncorrelated, suggesting that the dominant sources of these metals to house-dust—and/or their enrichment patterns—differ.

An extremely close relationship ($p<<0.001$) exists between the concentration (μg g^{-1}) of zinc in house-dust and the reciprocal of the dustiness ($mg^{-1}m^2$). This

relationship is shared by the cadmium concentration to a lesser extent ($p<0.05$) and not at all by copper and lead concentrations. It is also apparent that the amount ($\mu g\ m^{-2}$) of zinc is not very variable between houses, at an arithmetic mean value of 1 870 $\mu g\ g^{-1}$ and with an error on the mean (at a 95% confidence level) of only $\pm 160\ \mu g\ g^{-1}$ (Table 4·2). Assuming that a comparatively constant absolute quantity (μg) of zinc is to be found in each square metre of carpet (which is consistent with observation), and that the predominant source of this zinc is associated in some way with the carpet, the arrival of external zinc-low dusts would have the effect of lowering zinc concentrations ($\mu g\ g^{-1}$) in the carpet-dust. Thus, the existence of a dominant internal source of zinc would lead to the observed relationships. This internal source of zinc (and to a lesser extent cadmium) is probably the rubber of carpet backings and underlays (galvanized-iron would in most cases constitute an external source of zinc). Analyses were performed on three different types of rubber underlay material, and also on the rubber from a foam-rubber-backed carpet. All four materials have been commonly used by carpet-layers in Christchurch. The results are given in Table 4·5.

Table 4·5

Cadmium and zinc concentrations in rubber underlays and foam backings used under carpets.

Description		Mean concn ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	Coefficient of variation (%)[a]	Percent (%) of cadmium in the zinc[b]
Foam backing (n = 1)					
	Cadmium	0.496			0.068
	Zinc	726			
Rubber underlay #1					
(n = 2)	Cadmium	0.296	0.014	4.8	0.006
	Zinc	4 680	502	10.7	
Rubber underlay #2					
(n = 2)	Cadmium	0.173	0	0	0.034
	Zinc	508	25.5	5.0	
Rubber underlay #3					
(n = 2)	Cadmium	0.255	0.035	13.9	0.006
	Zinc	3 930	120	3.07	

Notes: **a.** 100[standard deviation/mean]
b. Assuming that all the cadmium in the rubber is associated with the zinc.

The data in Table 4·5 indicate firstly that rubber underlays or carpet backings can contain appreciable quantities of zinc, and secondly that the zinc used in these products appears to contain substantially less cadmium than is usual in zinc minerals (section 4·3·1)—and thus may have been purified. Ablation of the underlay or carpet backing is likely to occur during normal carpet use, causing the liberation of zinc-enriched particles. Dilution of these rubber fragments would be caused by the arrival (from other sources) of dusts with relatively low zinc concentrations, causing the observed relationship between zinc

concentrations and the reciprocal of the dustiness. The comparative weakness of the cadmium concentration–inverse dustiness relationship could be accounted for by the lower concentrations of cadmium found in the rubber carpet underlays and backings (relative to zinc minerals). Hence, the importance of this source of cadmium relative to other sources of the metal would be diminished.

The only other interesting relationship revealed by the correlation matrix is the positive and highly significant ($p<0.001$) one between the amount ($\mu g\ m^{-2}$) and the concentration ($\mu g\ g^{-1}$) of lead (Table 4·4). It is interesting to note that this relationship exists despite the fact that $\mu gPb\ g^{-1}$ is uncorrelated with the dustiness ($\mu gPb\ m^{-2}$ is highly correlated with dustiness). The relationship could reflect varying concentrations of lead in external dusts with house position. Assuming that a positive linear relationship exists between road-dust lead concentrations and traffic density (Fergusson *et al.* 1980), and if (on average) the same quantity of road-dust is transported to the interior of houses sited next to main roads on the occupants' footwear as is the cases of houses in quiet streets (which is cogitable), a linear relationship between the concentration and amount of lead in house-dust would be expected.

4·3·3 Sources of cadmium, copper, lead and zinc in house-dust

For each of the 120 houses surveyed, there were 18 measured variables. Some of these were continuous (*e.g.* metal concentrations, house age) and some were discrete (*e.g.* roof type, road type). The multidimensional nature of the data introduces problems when considering the effects of each variable in turn, as variables may themselves be (positively or negatively) influenced by other variables. For example, a direct comparison of the mean cadmium concentration of the wooden houses surveyed with that of the brick houses is not a simple comparison of wood versus brick, as the type of material used for house construction depends to a large extent upon the age of the house. Most of the wooden houses in Christchurch were built before about 1960, whereas most of the brick houses were built after that date. This type of direct comparison will only reveal trends in one dimension if they dominate—or complement—trends existing in other dimensions. The effect of this limitation is that it is easier (by this method) to identify a source than it is to discount the existence of one.

4·3·3a Factors influencing the amounts ($\mu g\ m^{-2}$) of the four metals

As was mentioned in the previous section (4·3·2) strong positive correlations exist between the amount ($\mu g\ m^{-2}$) of each of the four metals studied and the overall degree of dustiness. Consequently, several factors which might influence household dust levels were considered in turn. Table 4·6 is a summary of the mean dust levels listed under each variable's category.

Table 4·6

Mean levels, standard deviations and confidence limits of dustiness ($\mu g\ m^{-2}$) in terms of the categories of each of eight variables.

Variable	Category	Sub category (if applicable)	Sample size (n)	Mean dustiness ($mg\ m^{-2}$)	Standard deviation ($mg\ m^{-2}$)	Confidence interval (95%) ($mg\ m^{-2}$)[a]
Carpet usage	0 (new)		10	69.5	117	0–141
	1		35	212	309	110–314
	2		53	459	832	235–683
	3 (worn)		22	728	733	453–1000
Number of doors	1	0 outside	27	640	772	382–898
	2	0 outside	35	299	337	187–411
	2	1 outside	21	173	173	106–240
	3	0 outside	8	442	326	190–694
	3	1-2 outside	19	475	1 300	0–1 010
	4	1 outside	6	219	214	33–405
	5 or 6	1 outside	4	681	326	238–1 120
Fireplace	With		64	417	540	285–549
	Without		56	389	822	173–605
House material	Wood		66	547	865	338–756
	Brick		54	230	270	158–302
Roof type	Tile		57	528	874	301–775
	Galvanized-iron		56	260	314	178–342
	Other		7	550	926	0–1 290
Rubber underlay	With		63	316	746	132–500
	Without		57	501	598	346–656
Road type	0 (*cul de sac*)		10	500	835	0–1 010
	1		27	255	324	147–363
	2		38	503	980	191–815
	3		23	460	597	241–679
	4		14	209	262	80–338
	5 (main road)		8	494	266	303–685

Note: **a.** Student's t-test for $n<30$ and Normal distribution for $n\geq30$.

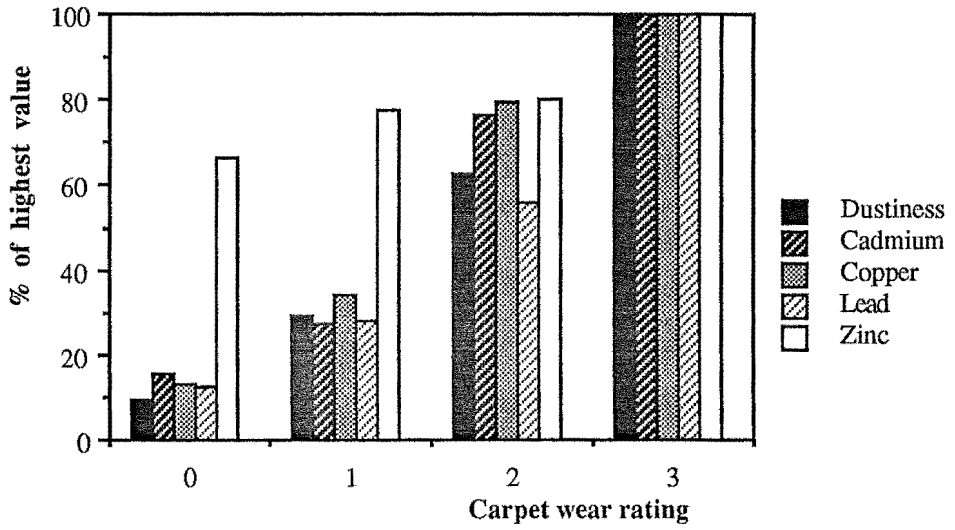
As can be seen from Table 4·6, most of the confidence intervals overlap. House age, the existence of a fireplace and the existence of a rubber carpet underlay can all be discarded in terms of having predictable effects on the dustiness. Contrary to expectations, it appears that dustiness does not increase with the number of doors to the room; neither is there any evidence which points to busier roads causing more dust in carpets. House material and roof type appear to have some effect. Wooden houses have on average 2.37 times more dust than brick ones (statistically significant) and houses with tiled roofs have on average 2.03 times more dust than those with roofs of galvanized-iron (not statistically significant).

However, the most important factor (among those measured) determining dustiness is carpet wear. A strong positive trend ($r = 0.991$, $p<0.01$) links dust levels with carpet

wear, apparently (and surprisingly) regardless of cleaning patterns. The flow-on effect that this trend has on the amounts of cadmium, copper, lead and zinc in house-dust is illustrated in Figure 4·3. Mean amounts (μg m^{-2}) of the four metals calculated for each carpet wear rating are given in Appendix 4·5.

Figure 4·3

The effect of carpet wear on the level of dust and on the relative amounts of cadmium, copper, lead and zinc in carpets. Quantities are graphed as a percentage of the mean value for threadbare carpets.



The tenfold increase in the mean dust level going from new to threadbare carpets results in an approximately sevenfold increase in the mean amounts of cadmium, copper and lead, and a smaller 150 percent increase in the mean amount of zinc. In summary, the dominating factor effecting the amounts (μg m^{-2}) of all four metals is the dustiness (mg m^{-2}), and the single most important factor (among those examined) which influences dustiness is likely to be the degree of carpet wear. A predicted worst scenario in terms of the amounts (μg m^{-2}) of cadmium and lead available to children would be a wooden house with (a tiled roof and) worn carpets.

4.3.3b Factors studied with respect to cadmium concentrations only

The use of cadmium sulphide and cadmium thioselenides in dying some textiles various shades of red, orange and yellow (Table 1·1) implies that some carpets may contain these pigments. However, direct comparison of the mean cadmium concentration for carpets coloured these shades (n = 37) with the mean for carpets without them (n = 83) revealed nothing of statistical significance (Table 4·7). Notwithstanding this, Principal Components Analysis did identify red, orange and yellow carpets as tending to have slightly more cadmium in them than carpets of other colours. This effect is small, and is discussed in more detail in section 4·3·3f.

Table 4·7

Mean cadmium concentrations and summary statistics relating to the various categories of variables considered with respect to cadmium concentrations only.

Variable	Category	Sub category (if applicable)	Sample size (n)	Mean [Cd] ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	Confidence interval (95%) ($\mu g\ g^{-1}$)[a]
Carpet colour	Red, orange or yellow		37	5.38	3.27	4.33–6.43
	Other colours		83	5.06	3.62	4.28–5.84
Number of doors	1	0 outside	27	5.28	3.30	4.18–6.38
	2	0 outside	35	5.15	3.81	0.99–9.31
	2	1 outside	21	5.84	4.33	4.17–7.51
	3	0 outside	8	6.71	4.63	3.13–10.3
	3	1-2 outside	19	4.03	1.94	3.24–4.82
	4	1 outside	6	4.52	1.96	2.82–6.22
	5 or 6	1 outside	4	4.36	3.19	0.03–8.69
Fireplace	With		64	4.54	2.87	3.84–5.24
	Without		56	5.85	4.02	4.80–6.90

Note: **a.** Student's t-test for $n<30$ and Normal distribution for $n\geq30$.

Household traffic patterns were expected to have some effect on the cadmium concentrations (through the introduction of foot-borne dirt). The number of doors leading into a room, the number of occupants in the house, and their habits all determine the frequency with which a particular piece of carpet is traversed. Of these, only the first parameter was measured in this survey. No clear trend is apparent from the data in Table 4·7 which links the cadmium concentrations with the number of doors to the room sampled. There are three possible reasons for this:

1. No relationship between household traffic patterns and cadmium concentrations exists;
2. The sample size of each sub-category was insufficient for trends to be revealed;
3. The number of occupants and/or their routines dominate the household traffic pattern term.

One of the major sources of atmospheric cadmium is combustion (section 1·3·1 and Chapter 7). It therefore seemed not unreasonable to suppose that a fraction of cadmium liberated in a house's fireplace may find its way to the carpet-dust of that house. No statistically significant difference, however, distinguishes the mean cadmium concentration in houses with fireplaces (n = 64) from that of houses without fireplaces (n = 56) (Table 4·7). There are two possible confounding factors in the direct comparison of houses with fireplace with other houses. Firstly, the former group were on average 10 years older (mean age 45 years) than the latter group (mean age 35 years), and secondly, the older houses were predominantly wooden, and the newer ones brick.

4.3.3c Factors effecting cadmium and zinc concentrations

The two variables (of those studied) with the potential to influence zinc (an hence cadmium) concentrations were roof type and rubber underlay existence. Mean concentrations of cadmium and zinc under the categories of each variable are given in Table 4·8.

Table 4·8

Mean concentrations (and summary statistics) of cadmium and zinc with respect to roof type and rubber underlay existence.

Metal concentration ($\mu g\ g^{-1}$)	Roof type			Rubber underlay	
	Tiled (n = 57)	Galvanized-iron (n = 56)	Other (n = 7)	With (n = 63)	Without (n = 57)
Cadmium					
Mean	5.11	5.43	3.25	5.30	4.99
Std. deviation	3.63	3.53	1.14	3.94	2.98
95% error on mean[a]	±0.94	±0.92	±0.90	±0.97	±0.77
Zinc					
Mean	18 100	26 100	15 400	31 000	11 050
Std. deviation	33 400	39 100	12 900	42 900	20 500
95% error on mean[a]	±8 700	±10 200	±10 200	±10 600	±5 300

Note: a. Student's t-test for n<30 and Normal distribution for n≥30.

Although the mean concentration of zinc in house-dust of homes with galvanized-iron roofs is 1.44 times higher than the value for houses with tiled roofs, the gap between the two groups is not statistically significant (Table 4·8). It is probable that the direct measurement of the difference in house-dust zinc concentrations between the two groups is to some extent confounded by zinc from houses with galvanized-iron roofing ending up in the carpet-dust of neighbouring houses with tiled roofs (where samples were then taken). If the difference actually reflects genuine enrichment of zinc in houses with galvanized-iron roofing, a similar magnitude flow-on effect to cadmium concentrations is lacking (a possible reason for which could be the purity of the zinc used in galvanizing (section 4·3·1)). Principal Components Analysis suggested that galvanized-iron roofing does in fact have a minor effect on house-dust cadmium concentrations (section 4·3·3f).

The mean concentration of zinc in the carpet-dust of houses with rubber carpet underlays or backings is 2.8 times higher than the figure for houses without them; in this case, the difference between the two means is statistically significant (Table 4·9). However, once again, the enhanced concentrations of zinc in houses with rubber underlays appears to have no effect on the cadmium concentrations in those houses. The relative purity of the zinc in rubber carpet underlays or backings (Table 4·5) is a possible reason for this.

4·3·3d Factors influencing cadmium and lead concentrations

The two likely sources of lead in house-dust are lead paint and lead associated with petroleum (Sayre and Katzel, 1979; Charney *et al.* 1980). The most common lead pigments used in paints are white ($2PbCO_3.Pb(OH)_2$, $2PbSO_4.PbO$, $PbO.SiO_2$ and $PbCO_3$), yellow (PbO and $PbCrO_4$) and orange ($PbCrO_4$, $Pb(OH)_2$ and $PbMoO_4$) (Sturges and Harrison, 1985). Tetra-methyl lead and tetra-ethyl lead are added to petroleum as aids to smooth combustion (Fergusson, 1986). Early indications were that lead paint can contain relatively high concentrations of cadmium. Seven lead paint samples (stripped from a house being re-painted) were analysed, and were found to contain a mean lead level of 146 000 $\mu g\ g^{-1}$ (standard deviation 41 500 $\mu g\ g^{-1}$) and a mean cadmium concentration of 101 $\mu g\ g^{-1}$ (standard deviation 31 $\mu g\ g^{-1}$). Summary statistics relating to the mean concentrations of cadmium and lead under the various categories of the variables "house material" and "paint colour" are given in Table 4·9.

Table 4·9

Mean concentrations (and summary statistics) of cadmium and lead under the categories of the variables house material and paint colour.

	House material		Paint colour					
	Wood	Brick	No paint	Yellow, orange, or red	White or cream	Blue	Green	Brown
Sample size	66	54	34	8	64	1	5	8
Cadmium								
Mean	5.01	5.32	4.94	4.50	5.66	6.50	3.53	3.48
Std. deviation	3.20	3.88	3.17	2.44	3.95		1.80	2.10
95% error on mean[a]	±0.077	±1.03	±1.07	±1.75	±0.97		±1.92	±1.50
Lead								
Mean	882	547	515	932	815	433	916	599
Std. deviation	682	337	270	929	619		911	355
95% error on mean[a]	±165	±90	±91	±665	±152		±971	±254

Note: a. Student's t-test for $n<30$ and Normal distribution for $n\geq30$.

Direct comparison of the mean house-dust lead concentration for wooden houses (some of which would have been painted with a lead-containing paint) with the mean value for brick houses (usually unpainted) reveals a statistically significant difference in house-dust lead concentrations between the two groups—wooden houses have significantly more house-dust lead than do brick houses. However, no significant difference is apparent in cadmium concentrations between samples taken from wooden houses and those collected from houses of brick (Table 4·9). Thus, although lead paint is implicated as a significant

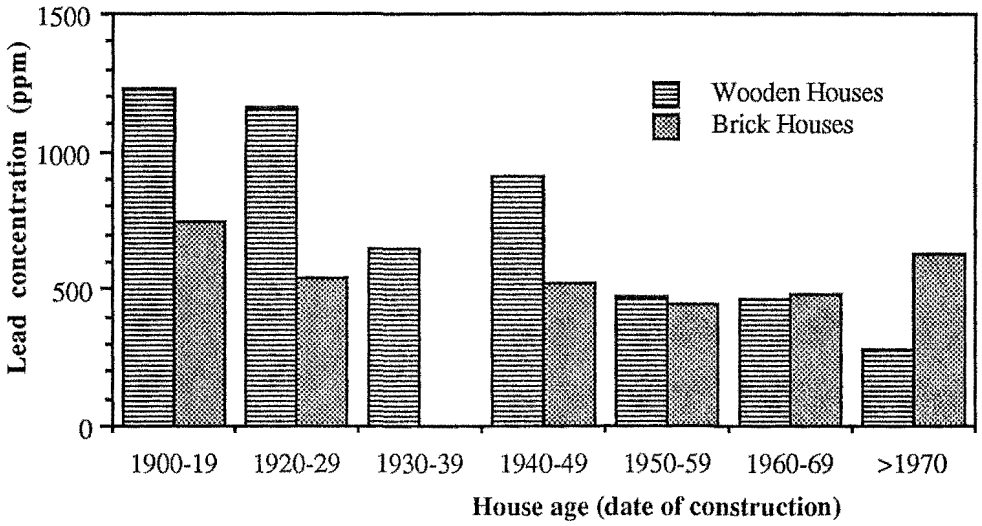
source of lead in house-dust, it does not appear (from this data) to be a significant source of cadmium.

Subdivision of the data according to paint colour (Table 4·9) yields no useful information; all confidence intervals overlap for both cadmium and lead concentrations. Although house colours which are consistent with the colours of lead pigments comprise 84% the painted house sample, it is probable that a significant number of these houses were painted with lead-free paint. In addition to this, red, orange, or yellow house colours could be due to the use of cadmium pigments or lead pigments (or neither), further complicating the interpretation of the direct comparison between paint colours.

A breakdown of the data with respect to house age and material (wood or brick) is given in Appendix 4·6. Figure 4·4 is constructed from the data in Appendix 4·6.

Figure 4·4

Mean concentrations (μg g^{-1}) of lead with respect to house age and material.



Before about 1950, lead house paint was widely used in Christchurch; after that date the practice was largely discontinued (Fergusson, 1988). It can be seen from Figure 4·4 (and Appendix 4·6) that the highest concentrations of lead are associated with the oldest wooden houses (built between 1900 and 1919). The mean concentration of lead in the house-dust of wooden houses decreases as the year of construction increases; in the case of brick houses a similar trend is not apparent. The data suggests both that lead paint is a significant source of lead in house-dust, and that if a house is lead-painted, the older the house, the greater the contribution the paint will make to the house-dust lead concentrations. This latter trend is likely to be linked to the condition of the paintwork on the older houses and also to the "painting history" of the house. For instance, the highest house-dust lead concentration found in this study (3 510 μg g^{-1}, Table 4·2) was at a house from which the old lead paint had been stripped 2–3 weeks prior to sampling. Another possible explanation for the trend observed in Table 4·4 is that the finer (lead-rich) particles have a longer time to

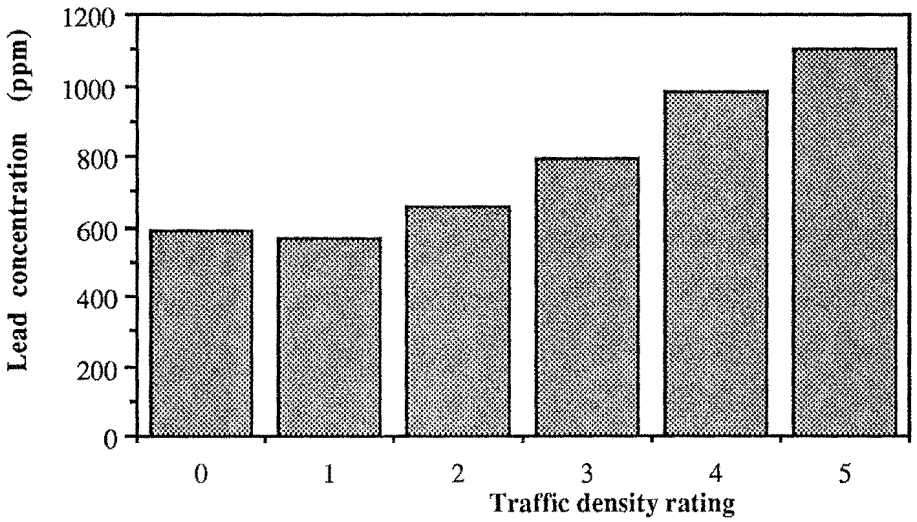
become selectively enriched in the older houses. However, this argument is weakened by the fact that carpets are usually replaced periodically (*e.g.* every 10–30 yr).

No trend was evident relating cadmium concentrations with house age (Appendix 4·6), once again indicating that lead paint is unlikely to constitute a significant source of cadmium in house-dust.

Traffic density was estimated on a scale of 0 (*cul de sac* or very quiet street) to 5 (main road). Summary statistics relating to the subdivision of the lead and cadmium concentration data on the basis of traffic density are given in Appendix 4·7, and Figure 4·5 is derived from the portion of this data relating to lead concentrations.

Figure 4·5

Mean house-dust lead concentrations in relation to traffic density.

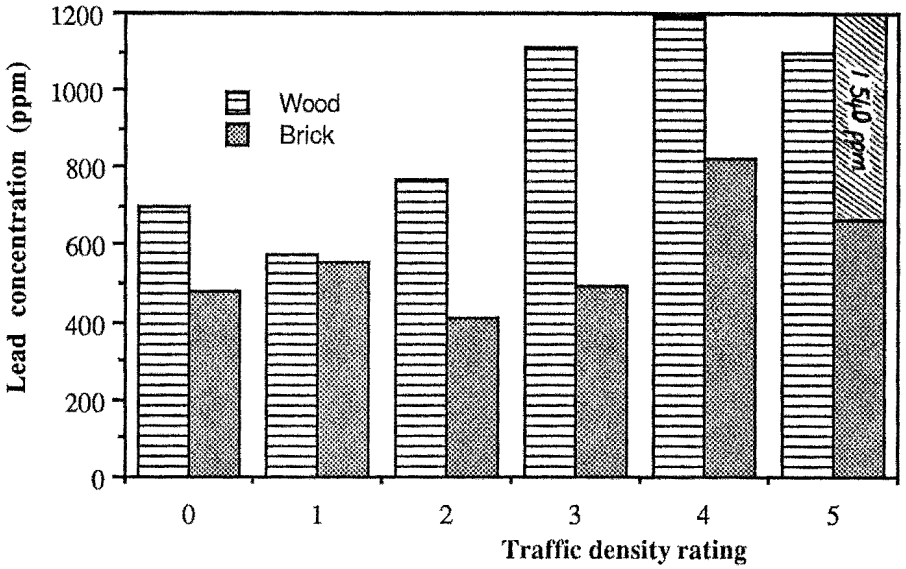


Considering the semi-qualitative nature of the traffic density estimate, a surprisingly linear relationship (F-test; $p = 0.003$) was found between house-dust lead concentrations and the traffic density ratings (Figure 4·5). The possibility that the oldest houses were predominantly sited near the busiest roads was examined, but no relationship was found to exist between house age and traffic density (Appendix 4·8). Thus, reasonable (circumstantial) evidence has been found suggesting that petrol lead contributes significantly to house-dust lead concentrations. On average, house-dust from houses sited next to main roads has twice the lead concentration as dust from houses located in "quiet" streets.

The results of further subdivision of the above data according to building material (wood or brick) are presented in Appendix 4·9, from which Figure 4·6 is derived.

Figure 4·6

Variations in the mean concentration of lead with respect to house material and the traffic density rating.



The following conclusions can be drawn from the data in Appendix 4·9 and from Figure 4·6:

1. Wooden houses have higher house-dust lead concentrations than brick houses irrespective of road type. This difference is presumably due to the use of lead-based paints on a significant proportion of the wooden houses.
2. For both wooden and brick houses a positive trend is apparent between lead concentrations and traffic density. Some loss of linearity (compared with Figure 4·5) is evident however, which is likely to be an artifact of the smaller sample sizes of each sub-category (and consequent loss of accuracy).
3. With the data resolved according to traffic density in this manner, the mean value of the difference between house-dust lead concentrations in wooden and in brick houses at each traffic density point can be calculated to be 411 μgPb g^{-1} (standard deviation 301 μgPb g^{-1}). This figure could be regarded as the likely minimum contribution that lead-based house paints make to Christchurch house-dust lead concentrations. (It would be a minimum because it is unlikely that all of the houses surveyed were lead painted.)

No clear relationship is apparent between house-dust cadmium concentrations and traffic density (Appendix 4·7), a fact which suggests that petrol lead is not a significant source of cadmium in house-dust.

4·3·3e Factors effecting all four metal concentrations

As window area (m^2) and house age (yr) are continuous variables, it was possible to derive correlation coefficients for the relationships between these parameters and the concentrations of cadmium, copper, lead and zinc. These are given in Table 4·10.

Table 4·10

Correlations between the concentrations of the four metals studied and both house age and the area of opening windows. Number of pairs = 120.

Correlated metal concentration ($\mu g\ g^{-1}$)	Area of opening windows (m^2)			Age of the house (years)		
	Correlation coefficient	Probability	Significance[a] of correlation	Correlation coefficient	Probability	Significance[a] of correlation
Cadmium	0.000	>0.1	Not	0.021	>0.1	Not
Copper	0.017	>0.1	Not	0.101	>0.1	Not
Lead	–0.099	>0.1	Not	0.442	<0.001	Highly
Zinc	–0.086	>0.1	Not	–0.185	>0.1	Not

Note: a. According to Pearson's tables.

A supposedly important factor influencing trace metal concentrations in house-dust is atmospheric fallout (Sayre and Katzel, 1979). However, the concentrations of cadmium, copper, lead and zinc are uncorrelated with the variable "window area". This finding does not necessarily detract from the importance of atmospheric fallout in determining the concentrations of these four metals; it may simply be an indication that window area is an inappropriate indicator of the extent of atmospheric fallout. The area of the opening widows in a room, for instance, may bear little relation to the number of windows actually opened by the occupants, or to the positions of the windows with respect to the most frequently prevailing winds.

Lead is the only metal concentration which shows a relationship with house age (Table 4·10). This relationship was discussed above (section 4·3·3d, Figure 4·4 and Appendix 4·6). The actual extent of the correlation falls into the "highly significant" category.

The effect of carpet wear on the concentrations of the metals studied is summarized in Table 4·11.

Table 4·11

Mean concentrations of cadmium, copper, lead and zinc with respect to the categories of the variable "carpet wear".

	Carpet wear rating			
	0 (new)	1	2	3 (threadbare)
Sample size	10	35	53	22
Cadmium				
Mean	10.3	4.39	4.74	5.00
Std. deviation	6.0	2.56	2.46	3.78
95% error on mean[a]	±3.66	±0.85	±0.66	±1.42

Table 4·11 continued...

	Carpet wear rating			
	0 (new)	1	2	3 (threadbare)
Copper				
Mean	266	193	186	161
Std. deviation	264	114	112	80
95% error on mean[a]	±161	±38	±30	±30
Lead				
Mean	1 070 (604[b])	613	658	903
Std. deviation	688 (130[b])	520	383	870
95% error on mean[a]	±420 (±107[b])	±172	±103	±327
Zinc				
Mean	81 700	30 500	11 300	5 560
Std. deviation	70 600	36 500	13 000	3 470
95% error on mean[a]	±43 100	±12 100	±3 500	±1 300

Notes: **a.** Student's t-test for n< 30, Normal distribution for n≥ 30.
b. With data for wooden houses over 70 years old (n = 4) removed.

The apparently high concentrations of cadmium and lead in new carpets (Table 4·11) may not reflect real differences, but may be a result of outliers exerting undue influence on the means due to the small sample size of houses with new carpets (n = 10). If data relating to old (≥70 years) wood houses are removed from the calculation, the mean lead concentration in houses with new carpets falls to 604 $\mu g\ g^{-1}$. This figure is more in keeping with the trend defined by the other three points. Similarly, 8 of the 10 houses with new carpets also had rubber underlays. If rubber underlays *were* in fact a source of cadmium (section 4·3·3c) the effect would be most noticeable in the houses with the least dust—that is, the houses with new carpets (section 4·3·3a).

If the data describing the mean lead and cadmium concentrations in houses with new carpets is ignored, two generalizations can be made from the remaining data in Table 4·11: firstly, that lead and cadmium concentrations increase with carpet wear; and secondly, that zinc and copper concentrations decrease with carpet wear (zinc more so than copper). A possible explanation for these observations in the cases of cadmium, lead and zinc can be made with recourse to the results of Johnson *et al.* (1982), who used Scanning Electron Microscopy and X-ray Energy Spectroscopy to characterize individual particles of house-dust. Among other things, they found that the highest concentrations of lead and cadmium were present in the finest particle size ranges; and (conversely) that zinc was the most enriched in the coarsest fractions (section 3·3·3c). Thus, for cadmium, lead and zinc, selective enrichment of the finer particle size ranges as the carpet becomes worn (concomitant with the relative "impoverishment" of the coarser size ranges) would account for the observed trends. This mechanism has already been proposed as a means by which house-dust trace metal concentrations may become elevated over those in garden soil (section 4·3·1;

Thornton *et al.* 1985). In addition to this, the fact that zinc concentrations diminish with carpet wear, and yet remain higher than external concentrations, suggests that the primary sources of zinc in house-dust are located within the house. One internal source of zinc which has already been identified (section 4·3·3c) is the rubber of carpet backings and rubber underlays.

In the case of copper, the observed trend (Table 4·11) is harder to rationalize. Copper and lead are the most highly correlated pair of metal concentrations, and it might therefore be expected that their enrichment patterns with carpet wear would be similar, not opposite. Sources of lead have been identified as lead-based paint and petrol lead (section 4·3·3d). Copper could be associated with either of these sources (as copper-containing paints and as copper metal or alloys of copper in cars). However, the dominant source of copper in house-dust may be entirely unrelated to sources of lead. Following the same reasoning as was used for zinc (above), the data in Table 4·11 would suggest that the dominant source of copper tends to produce relatively coarse particles, and may be located within the house.

4·3·3f Principal Components Analysis

Although sources of lead and zinc in house-dust were identified by direct comparison of the mean concentrations of lead and zinc for the various categories of each variable (sections 4·3·3c and 4·3·3d), this approach did not identify any sources of cadmium. A possible reason for this is that there are several minor but more or less "equal-weight" sources of cadmium in house-dust. Comparison of the mean cadmium concentrations relating to one source at a time does not take into account the effects of other sources.

The aim of multivariate data analysis is simplification. Principal Components Analysis (PCA) is a mathematical technique which can be used to reduce the dimensionality of a data matrix by creating new variables from groupings of old ones. It is of limited value if all the observed variables are more or less uncorrelated, and it has been recommended that at best, PCA should be viewed only as an approximation to reality (Gorsuch, 1983).

A PCA of the house-dust data relating to cadmium was carried out on a using a standard statistical software package ("Statview", Apple MacIntosh). The concentration of cadmium ($\mu g\ g^{-1}$) was entered as a continuous variable and "house age", "house material", "paint colour", "roof type", "rubber underlay existence", "carpet use", "carpet colour", "fireplace existence" and "road type" were entered as binary variables. Classifications of some of the binary variables are given in Appendix 4·1. The remaining variables were classified as follows: carpet colour: 1 = red, orange or yellow, 0 = other;

carpet wear: 1 = wear categories 2 and 3, 0 = wear categories 0 and 1;

house material: 1 = weatherboard, 0 = other;

paint colour: 1 = red, orange or yellow, 0 = other;

roof type: 1 = galvanized-iron, 0 = other.

Factor score weights of the "oblique transformation" solution of the PCA are given in Table 4·12.

Table 4·12

Factor score weights of the oblique transformation solution (Orthotran/Varimax) of the Principal Components Analysis of the data relating to cadmium in house-dust.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
µg Cd g^{-1}	0.002	–0.016	0.600	0.242	–0.105
House age	0.057	0.433	0.112	0.313	0.341
House material	0.090	0.519	–0.114	–0.031	–0.153
Paint colour	–0.063	0.440	0.107	–0.267	–0.051
Roof type	–0.071	–0.073	–0.032	0.582	–0.122
Rubber underlay	–0.474	–0.039	0.084	0.041	0.108
Carpet usage	0.520	0.040	0.005	–0.072	-0.113
Carpet colour	0.311	–0.070	0.246	0.411	0.187
Fireplace	0.006	–0.091	–0.604	0.335	–0.062
Road type	–0.116	–0.040	–0.056	–0.069	0.836

Five factors emerged from the calculation (Table 4·12). The first factor has high positive scores in the "carpet usage" and "carpet colours" rows and a high negative score in the "rubber underlay" row. This factor could therefore be re-labelled "carpet parameters". Similarly, the second factor could be re-labelled "housing parameters", and the fifth factor could be termed "road type", in view of the high positive score in that row. The third and fourth factors are more difficult to define in such a clear-cut manner; the fourth factor's scores are in the order roof type > carpet colour > fireplace existence > house age. These would probably reflect that fact that roof type and fireplace existence are dependent to a large extent on the age of the house. The third factor has the highest positive score of all factors in the µgCd g^{-1} row, and probably reflects the "bigness" of the cadmium concentration variable itself (Jollife, 1986).

Table 4·13 is derived from Table 4·12. Factors are re-labelled and factor score weights in Table 4·13 are assigned a positive or negative sign to indicate the nature of the influence exerted on each variable (score weights with values between –0.2 and 0.2 are omitted from the assignment). This approach is recommended by Jollife (1986).

Table 4·13

Simplified results of the Principal Components Analysis of the house-dust data.

	"Carpet parameters"	"Housing parameters"	"Bigness" of μgCd g^{-1}	"Roof type+"	"Road type"
μg Cd g^{-1}			+	+	
House age		+		+	+
House material		+			
Paint colour		+		−	
Roof type				+	
Rubber underlay	−				
Carpet usage	+				
Carpet colour	+		+	+	
Fireplace			−	+	
Road type					+

The three most important sources of cadmium implicated by these results (the variables which show the highest positive scores in columns where μgCd g^{-1} shows a positive factor score) are carpet colour, roof type and house age. ("Fireplace existence" shows both positive and negative effects on μgCd g^{-1}.) Thus, the highest concentrations of cadmium might be expected in old houses (pre 1950) with galvanized-iron roofs and red, orange and/or yellow shades in their carpets. However, the importance of these sources appears to be slight. Stepwise regression on the same data (using the cadmium concentration as the dependent variable) revealed that carpet colour, roof type and house age *when grouped together* accounted for only 16% of the total cadmium concentration variation, leaving 84% unaccounted for.

A test was made of the validity of this PCA interpretation by resorting to the original data. Each of the 120 houses was classified according to the number of the first three (potential) sources which applied to it (0–3). (For example, a house built before 1950, with a galvanized-iron roof but without red, orange or yellow tones in the carpet would be ranked "2".) On average, houses with all three factors were found to have more cadmium (6.77 μgCd g^{-1}) than those with any two factors (5.21 μgCd g^{-1}); which had more than those with any one factor (4.97 μgCd g^{-1}), which had more than those with none (4.89 μgCd g^{-1}). (Student's t-test 95% errors on means ± 1.14, ± 1.13, ± 1.21, ± 2.62 μgCd g^{-1}, respectively). Though the differences are not statistically significant, the trend is clear.

The association of cadmium with galvanized-iron roofing is presumably because of its presence in zinc; and the use of cadmium pigments in textile dyes (Table 1·1) could account for the carpet colour dependency. The actual source relating to house age is not clear, but cadmium impurity in lead paints is a possibility.

4·3·4 Summary of sources and influencing factors

A summary of the factors which were found to influence the concentrations (μg g^{-1}) and amounts (μg m^{-2}) of cadmium, copper, lead and zinc, and the level (mg m^{-2}) of dust in house-dust is given in Table 4·14.

Table 4·14

Summary of the sources or other factors influencing the level of dust and the concentrations and amounts of cadmium, copper, lead and zinc in house-dust.

Item	Source or factor which effects	Section reference
Dustiness (mg m^{-2})	Carpet wear (dominant factor). Increased dust with increased carpet wear	4·3·3a
	House material. Wood houses have on average 2.37 times more dust than brick houses (statistically significant)	4·3·3a
Amounts (μg m^{-2}) of Cd, Cu, Pb & Zn	Dustiness (highly significant correlation)	4·3·2
μgCd g^{-1}	PCA identified carpet colour, galvanized-iron roofing, and house age as having a minor effect	4·3·3f
	Carpet wear. Cd concentrations appear to increase with increasing carpet wear	4·3·3e
	Some sources of Cu, Pb and Zn are likely to contribute to Cd concentrations (correlations)	4·3·2
μgCu g^{-1}	Carpet wear. Cu concentrations decrease with increasing carpet wear	4·3·3e
	Highly correlated with μgPb g^{-1}	4·3·2
μgPb g^{-1}	Lead paint. Related to the age of the house and its material	4·3·3d & 4·3·3e
	Petrol lead. House-dust lead concentrations increase with increasing traffic density	4·3·2 & 4·3·3d
	Carpet wear. Pb concentrations appear to increase with increased carpet wear	4·3·3e
	Highly correlated with μgCu g^{-1} and μgPb m^{-2}	4·3·2

Table 4·14 continued...

Item	Source or factor which effects	Section reference
$\mu gZn\ g^{-1}$	Rubber carpet underlays. 2.8 times higher mean Zn concentration in houses with underlays (statistically significant)	4·3·2, 4·3·3c & 4·3·3e
	Carpet wear. Zn concentrations decrease with increased carpet wear	4·3·3e
	Dustiness. Zn concentrations decrease as dustiness increases (strong inverse correlation)	4·3·2
	Possibly galvanized-iron roofing (not statistically significant)	4·3·1 & 4·3·3c

No one source was found which predominated in determining the degree of enrichment of cadmium in house-dust. It is thought likely that several minor sources contribute to the concentrations of cadmium in house-dust; and that the effects of these are augmented by a selective enrichment process which operates in favour of the finer (cadmium-rich) dust particles (section 4·3·1).

4.4 Conclusion

The geometric mean cadmium concentration over the 120 houses surveyed was 4.24 $\mu g\ g^{-1}$ and the range was 0.557–21.0 $\mu gCd\ g^{-1}$. The average amount of cadmium absorbed by young children from ingested house-dust could represent about 0.4–4% of that typically adsorbed from food sources. No one dominant source of cadmium was identified, although several minor sources were implicated (section 4·3·4).

The geometric mean house-dust lead concentration was 573 $\mu g\ g^{-1}$. At such concentrations, lead in house-dust probably constitutes a significant extra source of lead to young children (in the worst scenario equalling the amount normally absorbed from food).

Petrol lead and lead-based paints were identified as significant sources of lead in house-dust, and rubber carpet underlays or backings were identified as a significant source of zinc. Correlations of cadmium with the other three metals imply that sources of copper, lead and zinc may also be sources of cadmium (although probably minor).

The amounts ($\mu g\ m^{-2}$) of all four metals were highly correlated with the overall dustiness ($mg\ m^{-2}$). Dustiness, in turn, was found to be predominantly determined by the degree of carpet wear (apparently regardless of cleaning patterns). Wooden houses also had more dust than brick ones.

Metal concentrations ($\mu g\ g^{-1}$) showed trends with carpet wear which suggested that selective enrichment of the finer particles in the carpet occurs with time.

4·5 References

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4·6 Appendices

Appendix 4·1 (section 4·2·1)

Variables and categories under which they were classified in the house-dust survey

Variable	Type of variable	How classified
Area of opening windows	Continuous	m^2
Carpet colour	Binary	0 (not red, orange or yellow)[a] 1 (red, orange or yellow)
Carpet wear	Discrete	0 (new) 1, 2, 3 (threadbare)
Doors: total in room	Discrete	Absolute number
Doors: total leading outside	Discrete	Absolute number
Fireplace	Binary	0 (no fireplace) 1(fireplace)
House age	Continuous	Years
House age	Binary	0 (built after 1950) 1 (built before 1950)
House material	Discrete	0 (brick or stone) 1 (weatherboard) 2 (painted concrete)[b] 3 (other material)
Paint colour	Discrete	0 (no paint)[c] 1 (red, orange or yellow) 2 (white or cream) 3 (blue) 4(green) 5(brown)
Roof type	Discrete	0 (tiled roof) 1 (galvanized-iron roof) 2 (other type of roof)
Rubber underlay	Binary	0 (no underlay) 1 (underlay)

Notes: **a.** Red, orange or yellow tones are consistent with cadmium pigments.
b. "Painted concrete" houses were usually plaster over weatherboard.
c. Usually red brick.

Appendix 4·2 (section 4·3·1)

Full data set of the house-dust survey. (See Appendix 4.1 for the meaning of each variable).

Suburb: St. Martins/Huntsbury (houses 1–8)

	House number							
	1	2	3	4	5	6	7	8
Mean values (n = 3)								
Dustiness mg m^{-2}	34.3	106	198	796	33.3	97.3	50.3	95.7
Cadmium µg g^{-1}	4.58	6.98	4.32	8.88	6.66	6.48	5.48	9.32
µg m^{-2}	0.127	0.728	0.727	7.06	0.208	0.622	0.263	0.768
Copper µg g^{-1}	198	174	154	187	242	162	239	211
µg m^{-2}	6.67	18.0	28.7	150	7.83	15.2	11.7	18.5
Lead µg g^{-1}	352	791	681	1 400	312	114	548	530
µg m^{-2}	14.0	80.0	133	1 120	10.0	12.5	26.7	46.5
Zinc µg g^{-1}	71 400	19 800	23 300	3 640	63 600	24 100	32 300	18 000
µg m^{-2}	1 920	2 080	2 280	2 890	2 120	2 090	1 430	1 340
Other variables								
House age(years)[a]	13	90	50	65	65	30	65	60
House material	0	1	1	2	1	0	1	1
Paint colour	0	2	1	2	2	0	2	1
Roof type	1	1	1	1	1	0	1	1
Rubber underlay	1	1	1	1	1	0	1	1
Carpet wear	1	1	1	2	2	1	0	0
Carpet colour	1	1	1	1	1	0	0	0
Fireplace	1	1	0	0	0	0	1	0
Doors:								
total in room	2	1	2	5	2	2	1	3
to outside	0	0	0	1	0	0	0	0
Window area (m^2)	2.23	1.67	1.30	0	0.28	0.74	1.39	1.12
Road type	0	1	1	2	3	2	2	2

Appendix 4·2 continued...

Suburb: St. Martins/Huntsbury (houses 9–15)					Bryndwr (house 16)			
	House number							
	9	10	11	12	13	14	15	16
Mean values (n = 3)								
Dustiness mg m^{-2}	310	151	140	21.7	35.8	81.5	9.81	327
Cadmium μg g^{-1}	14.6	3.28	2.19	6.83	14.6	1.86	21.0	2.66
μg m^{-2}	4.36	0.481	0.302	0.144	0.520	0.145	0.198	0.933
Copper μg g^{-1}	122	66.3	174	175	185	85.3	153	240
μg m^{-2}	38.5	9.80	23.9	3.80	6.60	6.93	1.53	78.3
Lead μg g^{-1}	546	101	261	572	743	478	464	729
μg m^{-2}	170	14.8	37.1	12.1	26.5	40.5	5.20	241
Zinc μg g^{-1}	5 220	12 200	11 300	71 600	43 100	18 500	205 000	6 620
μg m^{-2}	1 620	1 580	1 510	1 450	1 520	1 420	1 710	2 040
Other variables								
House age(years)[a]	60	14	12	7	60	40	20	41
House material	0	1	1	0	1	1	0	1
Paint colour	0	5	5	0	2	2	2	2
Roof type	0	1	2	1	1	0	1	0
Rubber underlay	1	1	1	1	1	1	1	1
Carpet wear	2	1	1	1	1	1	1	1
Carpet colour	1	0	0	1	0	0	0	0
Fireplace	0	1	0	0	0	1	0	1
Doors:								
total in room	3	1	2	2	1	2	2	2
to outside	0	1	1	1	1	1	0	0
Window area (m^2)	0.74	1.12	1.39	1.67	5.02	1.49	1.86	1.49
Road type	2	1	3	1	1	3	2	2

Appendix 4·2 continued...

Suburb: Bryndwr (houses 17–24)

	House number							
	17	18	19	20	21	22	23	24
Mean values (n = 3)								
Dustiness mg m^{-2}	444	293	1 050	345	1 030	1 490	456	198
Cadmium µg g^{-1}	2.43	0.557	2.05	3.40	2.69	3.06	6.66	2.69
µg m^{-2}	1.18	0.150	2.08	0.870	2.76	4.57	3.24	0.531
Copper µg g^{-1}	139	109	78.6	54.2	106	192	188	555
µg m^{-2}	60.2	31.7	83.7	18.3	109	285	86.0	110
Lead µg g^{-1}	244	594	610	177	398	636	445	297
µg m^{-2}	107	167	655	55.0	409	940	201	58.7
Zinc µg g^{-1}	5 260	6 720	2 370	6 200	3 810	1 330	4 800	8 210
µg m^{-2}	2 070	1 670	2 270	1 390	3 890	1 960	1 950	1 580
Other variables								
House age(years)[a]	29	50	30	38	35	30	40	45
House material	2	1	0	0	1	1	1	0
Paint colour	1	2	0	0	2	2	2	0
Roof type	0	1	0	0	0	0	0	0
Rubber underlay	1	1	1	0	0	0	0	1
Carpet wear	2	2	1	3	2	3	2	2
Carpet colour	0	0	1	0	0	0	0	1
Fireplace	0	1	1	0	1	1	1	0
Doors:								
total in room	2	2	5	1	1	2	1	2
to outside	0	0	1	0	0	2	0	0
Window area (m^2)	1.49	0.68	0	3.72	2.23	0.72	2.93	3.35
Road type	2	2	1	3	2	3	2	2

Appendix 4·2 continued...

Suburb: Bryndwr (houses 25–30)				Wainoni (houses 31–32)				
	House number							
	25	26	27	28	29	30	31	32
Mean values (n = 3)								
Dustiness mg m^{-2}	1540	221	516	5 680	220	12.6	203	564
Cadmium µg g^{-1}	1.71	4.69	6.37	4.71	1.53	6.24	5.98	7.35
µg m^{-2}	2.63	1.01	3.35	26.5	0.353	0.072	0.680	4.12
Copper µg g^{-1}	87.1	167	267	156	93.1	318	164	80.0
µg m^{-2}	133	36.7	138	886	21.4	3.93	33.8	44.8
Lead µg g^{-1}	242	1 130	681	719	264	1 220	372	769
µg m^{-2}	370	249	348	4 040	60.5	14.3	74.1	426
Zinc µg g^{-1}	1 490	7 770	3 450	871	8 360	153 000	9 250	3 120
µg m^{-2}	2 290	1 690	1 710	4 930	1 800	1 810	1 840	1 770
Other variables								
House age(years)[a]	40	60	33	40	32	31	37	10
House material	0	1	2	1	1	0	0	0
Paint colour	0	5	2	1	5	0	2	0
Roof type	0	1	0	0	0	1	0	0
Rubber underlay	0	0	0	1	1	1	0	1
Carpet wear	3	2	1	2	1	1	2	2
Carpet colour	1	1	0	0	0	0	1	1
Fireplace	0	0	1	0	1	1	1	1
Doors:								
total in room	1	2	3	1	1	2	2	3
to outside	0	1	0	2	0	0	0	1
Window area (m^2)	2.16	1.25	4.18	1.30	3.14	1.39	1.25	2.00
Road type	3	2	1	2	1	1	1	5

Appendix 4·2 continued...

Suburb: Wainoni (houses 33–40)

	House number							
	33	34	35	36	37	38	39	40
Mean values (n = 3)								
Dustiness mg m^{-2}	55.5	609	614	60.0	214	400	50.5	206
Cadmium µg g^{-1}	1.38	3.54	6.50	1.19	2.56	1.81	4.16	8.94
µg m^{-2}	0.068	2.32	3.95	0.069	0.547	0.767	0.203	1.77
Copper µg g^{-1}	152	316	182	195	194	115	387	130
µg m^{-2}	7.96	196	111	10.1	38.1	44.6	19.6	26.7
Lead µg g^{-1}	432	1 380	433	743	502	231	887	223
µg m^{-2}	23.4	858	269	39.7	101	91.6	44.2	45.7
Zinc µg g^{-1}	21 200	3 580	3 650	28 000	7 670	4 820	39 100	8 460
µg m^{-2}	1 030	2 150	1 990	1 180	1 510	1 870	1 960	1 720
Other variables								
House age(years)[a]	12	40	37	55	25	25	77	23
House material	0	2	1	1	0	0	1	0
Paint colour	0	2	3	5	2	0	2	0
Roof type	2	2	0	1	0	0	2	0
Rubber underlay	1	0	0	1	0	1	1	1
Carpet wear	2	2	3	1	2	2	1	1
Carpet colour	0	1	0	0	0	0	0	0
Fireplace	0	1	0	1	1	1	1	0
Doors:								
total in room	1	1	1	2	1	2	2	1
to outside	1	1	1	1	1	0	0	0
Window area (m^2)	1.12	2.23	1.81	2.37	2.23	1.72	1.58	2.51
Road type	2	5	2	1	3	4	4	3

Appendix 4·2 continued...

Suburb: Wainoni (houses 41–45)					Hoon Hay (houses 46–48)			
	House number							
	41	42	43	44	45	46	47	48
Mean values (n = 3)								
Dustiness mg m^{-2}	339	40.0	244	98.6	939	270	201	15.3
Cadmium µg g^{-1}	4.70	2.39	2.82	2.68	3.97	2.72	3.31	3.94
µg m^{-2}	1.32	0.096	0.688	0.256	3.72	0.799	0.633	0.055
Copper µg g^{-1}	184	147	155	173	88.4	68.3	238	352
µg m^{-2}	51.2	5.82	38.2	16.9	82.6	18.3	47.9	4.43
Lead µg g^{-1}	517	518	524	398	338	179	1 140	723
µg m^{-2}	144	20.9	128	38.3	318	48.6	231	9.26
Zinc µg g^{-1}	6 570	41 400	5 490	16 200	1 990	7 280	8 760	153 000
µg m^{-2}	1 770	1 650	1 340	1 560	1 850	1 870	1 750	1 780
Other variables								
House age(years)[a]	26	26	26	20	41	18	16	35
House material	0	2	0	0	1	0	0	1
Paint colour	2	2	0	4	2	2	0	2
Roof type	0	0	0	0	0	1	0	0
Rubber underlay	1	1	0	1	1	0	0	1
Carpet wear	2	1	3	2	3	3	2	1
Carpet colour	0	0	0	0	0	0	1	0
Fireplace	0	0	0	0	0	1	1	1
Doors:								
total in room	1	1	2	2	0	2	2	2
to outside	0	0	0	2	2	0	1	1
Window area (m^2)	1.12	1.25	0.84	1.12	0.93	1.86	1.67	1.86
Road type	3	2	5	2	2	2	1	1

Appendix 4·2 continued...

Suburb: Hoon Hay (houses 49–56)

	House number							
	49	50	51	52	53	54	55	56
Mean values (n = 3)								
Dustiness mg m^{-2}	49.2	82.2	138	115	128	278	419	339
Cadmium µg g^{-1}	4.63	6.62	4.72	8.94	7.29	2.18	4.76	1.97
µg m^{-2}	0.222	0.519	0.652	0.819	0.933	0.605	1.68	0.698
Copper µg g^{-1}	194	155	86.2	252	287	608	107	80.6
µg m^{-2}	9.41	13.6	11.8	30.1	37.0	168	43.6	26.8
Lead µg g^{-1}	234	582	151	353	867	788	355	496
µg m^{-2}	11.3	50.8	20.8	42.2	112	218	140	166
Zinc µg g^{-1}	31 300	16 000	9 840	13 400	10 600	4 780	3 660	3 920
µg m^{-2}	1 510	1 220	1 350	1 210	1 360	1 320	1 310	1 270
Other variables								
House age(years)[a]	13	33	26	26	17	40	18	30
House material	0	2	0	2	0	1	0	0
Paint colour	2	2	0	2	5	4	2	0
Roof type	1	0	1	1	1	0	1	0
Rubber underlay	1	1	1	1	0	0	1	0
Carpet wear	1	2	2	2	2	2	1	3
Carpet colour	0	0	0	1	1	0	0	0
Fireplace	0	1	0	1	0	0	0	1
Doors:								
total in room	1	1	2	1	2	5	2	1
to outside	1	1	2	0	1	1	0	1
Window area (m^2)	2.23	2.49	3.07	0.47	10.0	0	2.23	3.14
Road type	1	1	1	1	3	4	1	5

Appendix 4·2 continued...

Suburb: Hoon Hay (houses 57–60)				Upper Riccarton (houses 61–64)				
				House number				
	57	58	59	60	61	62	63	64
Mean values (n = 3)								
Dustiness mg m^{-2}	216	55.2	494	1 300	47.5	175	1 050	136
Cadmium µg g^{-1}	2.56	7.95	3.92	3.77	3.57	2.13	2.78	1.69
µg m^{-2}	0.623	0.438	1.93	4.95	0.171	0.370	2.79	0.230
Copper µg g^{-1}	171	350	228	212	199	113	166	135
µg m^{-2}	36.7	18.6	112	285	9.28	20.1	175	18.6
Lead µg g^{-1}	438	1 010	2 050	1 040	741	278	851	113
µg m^{-2}	94.5	55.5	1 020	1 400	35.5	50.7	915	15.2
Zinc µg g^{-1}	5 900	22 800	3 110	1 550	45 400	11 400	2 300	1 710
µg m^{-2}	1 180	1 180	1 540	2 010	2 070	1 830	2 380	1 710
Other variables								
House age(years)[a]	30	15	71	36	45	35	92	12
House material	0	0	1	1	0	0	1	2
Paint colour	0	0	2	2	2	0	2	2
Roof type	0	1	1	0	1	0	1	1
Rubber underlay	0	1	0	0	1	1	0	1
Carpet wear	2	1	3	2	1	2	2	1
Carpet colour	1	0	2	0	0	1	1	0
Fireplace	1	1	1	1	1	1	1	0
Doors:								
total in room	2	1	2	2	3	3	3	2
to outside	0	2	0	0	1	1	0	1
Window area (m^2)	1.86	5.53	1.39	1.12	6.50	1.86	0	2.93
Road type	3	4	4	0	3	1	2	2

Appendix 4·2 continued...

Suburb: Upper Riccarton (houses 65–72)

	House number							
	65	66	67	68	69	70	71	72
Mean values (n = 3)								
Dustiness mg m^{-2}	2 620	68.3	17.9	253	137	10.3	122	263
Cadmium µg g^{-1}	0.893	4.07	5.21	2.88	2.19	17.5	4.55	4.85
µg m^{-2}	2.13	0.281	0.094	0.777	0.301	0.134	0.597	1.28
Copper µg g^{-1}	94.2	139	347	130	139	203	106	176
µg m^{-2}	238	9.48	5.66	31.8	18.9	1.68	13.2	46.9
Lead µg g^{-1}	206	445	648	297	398	787	437	570
µg m^{-2}	536	30.4	11.4	74.8	54.5	7.12	53.9	150
Zinc µg g^{-1}	994	23 800	99 200	7 140	11 900	154 000	11 500	5 570
µg m^{-2}	2 480	1 620	2 010	1 680	1 480	1 490	1 290	1 450
Other variables								
House age(years)[a]	30	17	3	26	20	4	15	20
House material	2	0	2	0	0	0	0	0
Paint colour	1	0	5	2	0	2	0	0
Roof type	0	1	0	1	1	0	1	1
Rubber underlay	0	0	1	1	0	1	0	1
Carpet wear	3	2	1	1	2	0	2	2
Carpet colour	0	0	0	0	0	0	1	0
Fireplace	1	0	0	1	0	0	0	1
Doors:								
total in room	1	2	2	1	2	1	1	1
to outside	0	1	0	1	1	1	1	1
Window area (m^2)	3.34	0.93	0.84	1.05	1.39	1.39	2.09	1.86
Road type	0	1	0	0	4	0	0	2

Appendix 4·2 continued...

Suburb: Upper Riccarton (houses 73–75)				Linwood (houses 76–80)				
				House number				
	73	74	75	76	77	78	79	80
Mean values (n = 3)								
Dustiness mg m^{-2}	185	30.2	191	299	2 280	177	49.8	1 450
Cadmium µg g^{-1}	2.77	2.92	5.13	1.95	7.04	4.99	2.04	2.46
µg m^{-2}	0.517	0.089	0.965	0.573	15.8	0.889	0.103	3.32
Copper µg g^{-1}	111	141	203	245	424	110	123	174
µg m^{-2}	20.4	4.23	38.9	71.5	972	19.2	6.03	254
Lead µg g^{-1}	597	747	2 220	745	1 510	521	451	774
µg m^{-2}	111	21.5	429	219	3 340	92.7	23.2	1 110
Zinc µg g^{-1}	10 300	45 900	7 880	7 930	2 010	6 110	20 000	2 170
µg m^{-2}	1 900	1 350	1 460	2 340	4 520	1 070	921	2 760
Other variables								
House age(years)[a]	45	28	42	78	60	13	80	108
House material	0	0	1	0	2	0	2	2
Paint colour	0	0	2	0	2	0	2	5
Roof type	0	1	0	1	0	1	1	1
Rubber underlay	1	1	0	0	0	0	0	1
Carpet wear	2	1	2	3	2	2	1	1
Carpet colour	1	1	0	0	0	1	0	1
Fireplace	1	1	0	1	0	0	1	1
Doors:								
total in room	3	2	1	3	1	1	2	2
to outside	0	1	0	0	0	1	0	0
Window area (m^2)	2.14	1.49	4.46	2.23	1.63	3.53	1.14	1.39
Road type	3	2	2	3	3	0	3	1

Appendix 4·2 continued...

Suburb: Linwood (houses 81–88)

	House number							
	81	82	83	84	85	86	87	88
Mean values (n = 3)								
Dustiness mg m^{-2}	1 200	7.15	637	2 600	185	158	29.7	136
Cadmium µg g^{-1}	4.17	5.35	9.19	4.40	2.22	3.89	8.09	2.91
µg m^{-2}	5.26	0.038	5.57	11.2	0.427	0.625	0.259	0.395
Copper µg g^{-1}	238	1 010	154	127	122	112	232	121
µg m^{-2}	285	7.06	97.0	329	21.8	17.2	6.19	16.5
Lead µg g^{-1}	2 520	2 160	3 510	804	406	712	588	1 010
µg m^{-2}	3 070	15.1	2 220	2 090	73.3	112	17.3	140
Zinc µg g^{-1}	2 460	124 000	4 010	1 170	6 600	7 030	30 100	12 500
µg m^{-2}	2 920	855	2 530	3 010	1 110	1 080	781	1 600
Other variables								
House age(years)[a]	80	14	67	45	36	39	3	13
House material	2	0	1	1	1	0	0	0
Paint colour	4	2	2	1	4	2	0	2
Roof type	1	0	0	2	0	0	0	0
Rubber underlay	0	1	0	0	0	0	1	0
Carpet wear	3	0	3	3	3	2	1	3
Carpet colour	0	0	1	1	0	1	0	1
Fireplace	1	1	1	1	0	0	0	0
Doors:								
total in room	1	1	3	1	1	2	1	1
to outside	0	1	0	0	0	0	1	1
Window area (m^2)	0.93	2.09	0.66	1.25	1.72	0.70	1.30	0.38
Road type	3	4	3	2	0	4	4	4

Appendix 4·2 continued...

Suburb: Linwood (houses 89–90)			St. Albans (houses 91–96)					
			House number					
	89	90	91	92	93	94	95	96
Mean values (n = 3)								
Dustiness mg m^{-2}	88.4	133	623	515	54.3	59.6	136	910
Cadmium µg g^{-1}	4.20	2.51	5.56	4.47	5.62	6.56	10.3	8.41
µg m^{-2}	0.393	0.296	3.53	2.31	0.291	0.300	1.42	7.67
Copper µg g^{-1}	175	105	216	94.2	117	116	140	214
µg m^{-2}	15.2	13.2	135	48.2	6.74	6.75	19.4	197
Lead µg g^{-1}	420	613	3 100	309	482	527	449	858
µg m^{-2}	36.4	79.9	1 910	158	27.0	29.9	61.1	787
Zinc µg g^{-1}	19 200	15 700	4 770	5 810	28 200	27 300	11 900	3 610
µg m^{-2}	1 560	1 590	2 960	2 960	1 440	1 330	1 650	3 280
Other variables								
House age(years)[a]	14	80	70	32	13	23	60	27
House material	0	1	1	1	0	2	2	0
Paint colour	2	2	1	2	2	0	2	0
Roof type	0	0	1	0	1	1	1	0
Rubber underlay	0	1	1	0	1	1	0	0
Carpet wear	2	1	1	2	2	2	3	2
Carpet colour	1	0	0	1	1	0	0	0
Fireplace	1	0	1	0	0	1	1	0
Doors:								
total in room	1	1	1	1	3	2	2	1
to outside	0	0	0	0	1	1	0	0
Window area (m^2)	2.56	1.12	0.42	3.11	1.12	0.49	1.25	1.95
Road type	1	4	5	1	4	5	2	5

Appendix 4·2 continued...

Suburb: St. Albans (houses 97–104)

	House number							
	97	98	99	100	101	102	103	104
Mean values (n = 3)								
Dustiness mg m^{-2}	304	135	644	177	316	447	79.9	276
Cadmium µg g^{-1}	7.23	4.05	6.49	8.62	4.16	16.8	12.8	7.03
µg m^{-2}	2.23	0.547	4.19	1.63	1.32	7.63	0.856	1.97
Copper µg g^{-1}	255	92.1	123	131	65.0	326	169	123
µg m^{-2}	76.3	11.8	78.9	23.1	20.5	148	13.3	33.8
Lead µg g^{-1}	677	964	513	574	619	1 530	341	1 210
µg m^{-2}	204	127	324	102	195	708	24.4	358
Zinc µg g^{-1}	7 110	3 230	9 610	10 200	10 900	6 420	23 900	9 190
µg m^{-2}	2 130	404	7 300	1 710	3 380	2 970	1 560	2 440
Other variables								
House age(years)[a]	23	80	35	50	17	65	30	47
House material	0	1	1	1	0	2	0	2
Paint colour	0	2	2	2	2	2	0	2
Roof type	1	1	0	0	2	0	0	0
Rubber underlay	0	0	0	0	0	0	1	0
Carpet wear	2	2	3	3	2	3	1	2
Carpet colour	0	0	0	1	1	1	0	0
Fireplace	1	1	1	0	0	1	1	0
Doors: total in room to outside	2	2	1	1	1	1	1	2
Window area (m^2)	4.88	1.67	2.44	4.55	4.18	3.48	2.51	1.67
Road type	1	1	2	1	3	2	2	0

Appendix 4·2 continued...

Suburb: St. Albans (house 105)	Sydenham (houses 106–112)							
	House number							
	105	106	107	108	109	110	111	112
Mean values (n = 3)								
Dustiness mg m^{-2}	51.9	394	274	59.9	385	600	78.2	314
Cadmium µg g^{-1}	7.24	5.50	7.56	5.22	9.06	4.34	2.95	1.99
µg m^{-2}	0.371	2.17	2.07	0.312	3.51	2.64	0.224	0.647
Copper µg g^{-1}	126	209	632	215	343	178	88.4	114
µg m^{-2}	6.12	83.0	170	12.4	133	107	6.39	35.4
Lead µg g^{-1}	1 260	1 360	639	761	606	1 170	240	744
µg m^{-2}	57.9	533	173	44.7	232	746	20.6	236
Zinc µg g^{-1}	32 400	6 960	12 000	26 400	7 500	4 230	20 700	6 220
µg m^{-2}	1 550	2 700	3 210	1 510	2 860	2 500	1 270	1 920
Other variables								
House age(years)[a]	70	70	20	60	20	114	4	80
House material	1	1	0	1	0	1	0	1
Paint colour	2	2	2	2	2	1	0	2
Roof type	0	1	1	1	1	1	2	1
Rubber underlay	0	1	0	0	0	1	1	1
Carpet wear	0	0	1	2	3	1	1	2
Carpet colour	0	0	0	1	0	0	0	0
Fireplace	1	1	0	1	0	1	0	1
Doors:								
total in room	1	3	1	2	2	4	3	2
to outside	0	1	0	0	0	1	1	0
Window area (m^2)	1.65	1.95	1.46	0.58	0.70	4.18	4.18	1.86
Road type	3	2	2	2	1	5	3	2

Appendix 4·2 continued...

Suburb: Sydenham (houses 113–120)

	House number							
	113	114	115	116	117	118	119	120
Mean values (n = 3)								
Dustiness mg m^{-2}	64.3	647	968	130	50.6	8.32	31.3	290
Cadmium µg g^{-1}	2.14	5.43	6.40	2.58	3.20	13.7	3.34	3.00
µg m^{-2}	0.135	3.81	4.95	0.337	0.159	0.114	0.093	0.890
Copper µg g^{-1}	138	476	166	85.6	109	172	147	248
µg m^{-2}	8.69	31.6	14.1	11.1	5.45	1.41	4.24	73.7
Lead µg g^{-1}	553	744	469	205	197	550	2 320	1 920
µg m^{-2}	35.9	48.1	39.0	26.7	9.43	4.55	65.4	553
Zinc µg g^{-1}	20 100	5 390	3 630	10 500	26 600	155 000	46 000	6 530
µg m^{-2}	1 270	309	326	1 360	1 310	1 280	1 240	1 850
Other variables								
House age(years)[a]	11	41	40	11	20	10	45	25
House material	2	1	1	1	0	1	2	1
Paint colour	2	2	4	2	2	2	2	2
Roof type	1	1	1	1	0	1	1	1
Rubber underlay	0	0	1	0	1	0	1	0
Carpet wear	1	2	2	2	1	0	0	3
Carpet colour	0	0	0	0	0	0	0	0
Fireplace	1	1	0	1	0	0	1	0
Doors:								
total in room	1	2	2	1	1	2	2	2
to outside	0	0	0	1	1	0	0	0
Window area (m^2)	1.12	1.58	0.84	1.63	0.70	0.84	0	0.56
Road type	3	3	4	2	2	2	4	2

Note: **a.** House age at the time of the survey (1987).

Appendix 4·3

Breakdown of the house-dust survey data according to suburb.

	Arithmetic mean	Standard deviation	95% error on mean[a]	Minimum value	Maximum value	Median
Suburb # 1 St.Martins/ Huntsbury						
Dustiness						
mg m^{-2}	144	197	±51	9.81	796	95.7
Cadmium						
µg g^{-1}	7.80	5.28	±1.36	1.86	21.0	6.66
µg m^{-2}	1.11	1.95	±0.50	0.127	7.06	0.481
Copper						
µg g^{-1}	169	49	±13	66.3	242	174
µg m^{-2}	23.2	36.5	±9.4	1.53	150	11.7
Lead						
µg g^{-1}	526	317	±82	101	1 400	530
µg m^{-2}	117	282	±73	5.20	1 120	26.7
Zinc						
µg g^{-1}	41 500	50 600	±13 100	3 640	205 000	23 300
µg m^{-2}	1 800	428	±110	1 340	2 890	1 620
House age (yr)	43.4	25.7	±6.7	7	90	50
Suburb # 2 Bryndwr						
Dustiness						
mg m^{-2}	922	1 400	±361	12.6	5 680	444
Cadmium						
µg g^{-1}	3.43	1.89	±0.49	0.557	6.66	2.69
µg m^{-2}	3.35	6.55	±1.69	0.072	26.5	1.18
Copper						
µg g^{-1}	183	127	±33	54.2	555	156
µg m^{-2}	139	218	±56	3.93	886	83.7
Lead						
µg g^{-1}	559	314	±81	177	1 220	594
µg m^{-2}	528	1 000	±259	14.3	4 040	241
Zinc						
µg g^{-1}	14 700	38 300	±9 900	871	153 000	5 260
µg m^{-2}	2 200	949	±245	1 390	4 930	1 950
House age (yr)	38.3	8.6	±2.2	29	60	38

Appendix 4·3 continued...

	Arithmetic mean	Standard deviation	95% error on mean[a]	Minimum value	Maximum value	Median
Suburb # 3 Wainoni						
Dustiness						
mg m^{-2}	309	267	±69	40	939	214
Cadmium						
µg g^{-1}	4.00	2.30	±0.60	1.19	8.94	3.54
µg m^{-2}	1.37	1.47	±0.38	0.068	4.12	0.688
Copper						
µg g^{-1}	177	80	±21	80	387	164
µg m^{-2}	48.5	49.7	±12.8	5.82	196	38.1
Lead						
µg g^{-1}	551	296	±77	223	1 380	502
µg m^{-2}	175	224	±58	20.9	858	91.6
Zinc						
µg g^{-1}	13 400	13 100	±3 390	1 990	41 400	7 670
µg m^{-2}	1 680	309	±80	1 030	2 150	1 770
House age (yr)	32.0	17.0	±4.4	10	77	26
Suburb # 4 Hoon Hay						
Dustiness						
mg m^{-2}	273	316	±82	15.3	1 300	201
Cadmium						
µg g^{-1}	4.62	2.16	±0.56	1.97	8.94	3.94
µg m^{-2}	1.04	1.18	±0.31	0.055	4.95	0.663
Copper						
µg g^{-1}	226	139	±36	68.3	608	212
µg m^{-2}	57.5	76.5	±19.8	4.43	285	30.1
Lead						
µg g^{-1}	694	494	±128	151	2 050	582
µg m^{-2}	241	406	±105	9.26	1 400	94.5
Zinc						
µg g^{-1}	19 700	37 300	±9 750	1 550	153 000	8 760
µg m^{-2}	1 460	273	±71	1 180	2 010	1 350
House age (yr)	28.3	14.6	±3.8	13	71	26

Appendix 4·3 continued...

	Arithmetic mean	Standard deviation	95% error on mean[a]	Minimum value	Maximum value	Median
Suburb # 5 Upper Riccarton						
Dustiness						
mg m^{-2}	354	675	±174	10.3	2 620	137
Cadmium						
µg g^{-1}	4.21	3.90	±1.01	0.893	17.5	2.92
µg m^{-2}	0.715	0.796	±0.206	0.089	2.79	0.370
Copper						
µg g^{-1}	160	62.7	±16.2	94.2	347	139
µg m^{-2}	43.5	68.4	±17.7	1.68	238	18.9
Lead						
µg g^{-1}	622	496	±128	113	2 220	570
µg m^{-2}	166	260	±67	7.12	915	53.9
Zinc						
µg g^{-1}	30 000	42 800	±11 000	994	154 000	11 500
µg m^{-2}	1 750	362	±93	1 290	2 480	1 680
House age (yr)	28.9	22.1	±5.7	3	92	26
Suburb # 6 Linwood						
Dustiness						
mg m^{-2}	629	854	±220	7.15	2 600	177
Cadmium						
µg g^{-1}	4.36	2.25	±0.58	1.95	9.19	4.17
µg m^{-2}	3.01	4.71	±1.22	0.038	15.8	0.573
Copper						
µg g^{-1}	231	231	±60	105	1 010	154
µg m^{-2}	142	255	±66	6.03	972	19.2
Lead						
µg g^{-1}	1 120	918	±237	406	3 510	745
µg m^{-2}	843	1 210	±313	15.1	3 340	112
Zinc						
µg g^{-1}	17 400	30 600	±7 900	1 170	124 000	7 030
µg m^{-2}	1 910	1 070	±277	781	4 520	1 590
House age (yr)	48.7	32.8	±8.5	3	108	45

Appendix 4·3 continued...

	Arithmetic mean	Standard deviation	95% error on mean[a]	Minimum value	Maximum value	Median
Suburb # 7 St. Albans						
Dustiness						
mg m^{-2}	315	262	±67.5	51.9	910	276
Cadmium						
µg g^{-1}	7.69	3.44	±0.88	4.05	16.8	7.03
µg m^{-2}	2.42	2.41	±0.62	0.291	7.67	1.63
Copper						
µg g^{-1}	154	70.2	±18.1	65.0	326	126
µg m^{-2}	55.0	60.3	±15.6	6.12	197	23.1
Lead						
µg g^{-1}	894	709	±183	309	3 100	619
µg m^{-2}	338	495	±128	24.4	1 910	158
Zinc						
µg g^{-1}	13 000	9 820	±2 540	3 230	32 400	7 300
µg m^{-2}	2 470	1 590	±409	404	7 300	2 130
House age (yr)	42.8	21.8	±5.63	13	80	35
Suburb # 8 Sydenham						
Dustiness						
mg m^{-2}	286	278	±72	8.32	968	274
Cadmium						
µg g^{-1}	5.09	3.15	±0.81	1.99	13.7	4.34
µg m^{-2}	1.47	1.61	±0.42	0.093	4.95	0.650
Copper						
µg g^{-1}	221	153	±40	85.6	632	172
µg m^{-2}	46.5	54.0	±13.9	1.41	170	14.1
Lead						
µg g^{-1}	832	617	±159	197	2 320	639
µg m^{-2}	184	237	±61	4.55	746	48.1
Zinc						
µg g^{-1}	23 900	38 100	±9 840	3 630	155 000	10 500
µg m^{-2}						
House age (yr)	60.8	34.2	±8.8	4	114	70

Note: a. Student's t-test.

Appendix 4·4 (section 4·3·2)

Correlation matrix for the house-dust data. Each figure represents 120 data pairs.
For 118 degrees of freedom, the following probability values are associated with each coefficient:
>0.298, p<0.001; 0.237-0.298, p<0.01; 0.215-0.237, p<0.02; 0.182-0.215, p<0.05.

	ln[dustiness]	ln[metal concn (μg g^{-1})]				ln[amount of metal (μg m^{-2})]			
	(mg m^{-2})	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
ln[dustiness (mg m^{-2})]	1	–0.205	–0.162	0.077	–0.963	0.891	0.913	0.873	0.423
ln [metal concn μg g^{-1}]									
Cd		1	0.294	0.254	0.267	0.257	–0.108	–0.077	0.060
Cu			1	0.464	0.210	–0.017	0.186	0.038	0.001
Pb				1	–0.053	0.200	0.252	0.510	0.127
Zn					1	–0.829	–0.870	–0.841	–0.258
ln[metal amount (μg m^{-2})] Cd						1	0.855	0.830	0.447
Cu							1	0.912	0.543
Pb								1	0.527
Zn									1

Appendix 4·5 (section 4·3·3)

The effect of carpet wear on the mean amounts of cadmium, copper, lead and zinc in carpets. (Errors on the mean are calculated using the Student's t-test for n<30, and the Normal distribution for n≥30.)

μg Metal m^{-2}	Carpet wear rating			
	0 (new) (n = 10)	1 (n = 35)	2 (n = 53)	3 (threadbare) (n = 22)
Cadmium				
Mean	0.467	0.806	2.25	2.94
Std. deviation	0.639	1.02	4.28	2.73
95% error on mean	±0.390	±0.338	±1.15	±1.02
Copper				
Mean	14.2	36.8	85.4	107
Std. deviation	24.7	56.9	179	96
95% error on mean	±15.1	±18.9	±48	±36
Lead				
Mean	78.7	174	347	620
Std. deviation	161	385	732	813
95% error on mean	±98.4	±128	±197	±305
Zinc				
Mean	1 510	1 760	1 820	2 270
Std. deviation	480	540	900	1 260
95% error on mean	±290	±180	±240	±470

Appendix 4·6 (section 4·3·3d)

Mean concentrations (and summary statistics) of concentrations (μg g^{-1}) of cadmium and lead with respect to house age and material.

Year of construction	Sample size		Statistic	Cadmium concentration (μg g^{-1})		Lead concentration (μg g^{-1})	
	Wood[a]	Brick		Wood[a]	Brick	Wood[a]	Brick
1900–1919	19	1	Mean	4.54	1.95	1 230	745
			Std. devn.	2.76		780	
			95% error[b]	±1.13		±320	
1920–1929	12	1	Mean	8.63	14.6	1 160	546
			Std. devn.	3.81		833	
			95% error[b]	±2.06		±450	
1930–1939	4	0	Mean	3.67		648	
			Std. devn.	3.68		79	
			95% error[b]	±5.00		±107	
1940–1949	10	5	Mean	4.21	2.93	911	518
			Std. devn.	1.75	0.85	563	234
			95% error[b]	±1.07	±0.91	±344	±249
1950–1959	14	9	Mean	3.83	3.85	474	450
			Std. devn.	1.98	2.03	239	327
			95% error[b]	±0.97	±1.33	±117	±220
1960–1969	3	16	Mean	5.96	6.30	466	488
			Std. devn.	3.32	4.91	98	198
			95% error[b]	±6.85	±2.23	±202	±90
>1970	4	22	Mean	3.09	5.38	281	628
			Std. devn.	1.56	3.25	255	438
			95% error[b]	±2.11	±1.22	±346	±164

Notes: **a.** "Wood" includes plaster over weatherboard.
b. Student's t-test error on mean.

Appendix 4·7 (section 4·3·3d)

Mean concentrations (μg g^{-1}) of cadmium and lead with respect the to traffic density rating. A rating of 0 corresponds to a *cul de sac* or a very quiet street, and a rating of 5 to a main road.

	Traffic density rating					
	0	1	2	3	4	5
Number in sample	10	27	38	23	14	8
Cadmium (μg g^{-1})						
Mean	5.36	5.28	5.88	4.24	4.31	5.07
Std. deviation	4.60	2.87	4.62	2.36	2.08	2.28
95% error on mean[a]	±2.81	±0.96	±1.47	±0.86	±1.02	±1.63

Appendix 4·7 continued...

	Traffic density rating					
	0	1	2	3	4	5
Lead (μg g^{-1})						
Mean	590	569	657	789	980	1 100
Std. deviation	330	280	476	786	688	870
95% error on mean[a]	±202	±94	±151	±288	±338	±62

Note: a. Student's t-test.

Appendix 4·8 (section 4·3·3d)

Mean traffic density rating for each class of house age.

Year of construction	Sample size	Mean traffic density rating	Standard deviation	95% error on mean[a]
1900–1919	20	2.90	1.30	±0.52
1920-1929	14	2.14	0.67	±0.33
1930–1939	3	1.33	0.58	±1.19
1940–1949	15	2.60	1.18	±0.56
1950–1959	23	1.61	1.16	±0.42
1960–1969	19	2.53	1.50	±0.61
>1970	26	2.00	1.55	±0.53

Note: a. Student's t-test.

Appendix 4·9 (section 4·3·3d)

Mean concentrations (μg g^{-1}) of lead with respect the to traffic density rating and house material. (A rating of 0 corresponds to a *cul de sac* or a very quiet street, and a rating of 5 to a main road.)

	Traffic density rating					
	0	1	2	3	4	5
Wood houses						
Sample size	5	14	26	11	6	4
Mean μgPb g^{-1}	702	579	771	1 110	1 190	1 540
Std. deviation	421	240	525	1 040	790	1 100
95% error on mean[a]	±449	±118	±183	±600	±710	±1 490
Brick houses						
Sample size	5	13	12	12	8	4
Mean μgPb g^{-1}	479	558	410	492	824	662
Std. deviation	192	327	195	233	606	179
95% error on mean[a]	±205	±168	±106	±126	±434	±243

Note: a. Student's t-test.

CHAPTER 5
CADMIUM IN COMMERCIAL PRODUCTS

5·1 Introduction

Although cadmium and its compounds are used extensively in the manufacture of commercial products (section 1·2), there have been few studies published in New Zealand in which potential sources of cadmium to the end-user associated with cadmium-containing products have been examined (section 2·2·2d). Of the items listed in Table 1·1, members of the non-occupationally exposed population are most likely to be found near cadmium-pigmented products (which include plastics, rubbers, ceramic glazes, dyes, paints and inks), plastics stabilized with cadmium compounds, nickel-cadmium batteries, and television sets. Nickel-cadmium batteries and television tubes are sealed, and as such the cadmium in these products is unlikely to constitute a direct risk to public health while the items are in use (although later disposal may cause some problems). The most commonly used cadmium pigments are cadmium sulphide (CdS) (used to colour items bright yellow) and cadmium thioselenide ($CdS_xSe_{(1-x)}$) (used for orange and red shades) (section 1·2; Förstner, 1980; Gmelin, 1959; Nriagu, 1980).

The aims of this section of the work were as follows:

1. to identify commercial products which contain high concentrations of cadmium;
2. to identify the chemical forms of cadmium in some of these products;
3. to gauge the extent of any potential health-risks associated with the use of cadmium in commercial products.

5·2 Method

Samples of ceramic glazes, crayons, paints, plastics, rubber products, fertilizer and coke were either purchased, or collected from the author's home, associates' homes or the laboratory. Slices of rubber were cut from a range of car tyres being discarded by a Christchurch firm, with a stainless-steel razor-blade. A sample of red printers' ink was donated by a Christchurch printery. Of the pigmented products collected, items coloured red, orange or yellow (colours consistent with those of cadmium pigments) predominated; in some cases products of other colours were collected for purposes of comparison.

Between 0.02 and 10 g of each sample was accurately weighed into 100 ml beakers (some plastic samples were cut to the desired size with a razor-blade or a pair of tin-snips). Most samples were ashed overnight at 425 °C. This relatively low ashing temperature was chosen because of cadmium's volatility (section 1·1) (although many of the commercially-used cadmium compounds actually have melting and boiling points considerably higher than those of metallic cadmium). Water-based paints, ceramic glazes and the cadmium alloy were

not ashed. The raw samples or ashes were boiled in 15 ml of 4 M nitric acid (AR) for 30 minutes. Each solution was filtered through an acid and double-distilled water washed Whatman No. 540 filter paper into a 25 ml volumetric flask. The residue was washed with double-distilled water until a total solution volume of 25 ml was reached.

FAAS with background correction was used for the analysis of digestion extracts for cadmium, and in some cases zinc and selenium (parameters are given in Chapter 14). Standards were prepared from 1 000 $\mu g\ ml^{-1}$ stock solutions. In the majority of cases samples were analysed once only; however, 21 products found to have high concentrations of cadmium were each analysed several times.

The variability in sample composition (fertilizer, paint, plastic, rubber, *etc.*) and lack of any certified reference materials possessing similar matrices made it difficult to assess the analytical bias of the results. Nevertheless, a sample of the spiked Tai Tapu silt loam mentioned in section 3·3·1 was included with most batches of samples analysed. The mean concentration of cadmium for 13 separate analyses of this sample was 36.4 $\mu g\ g^{-1}$ (standard deviation 2.6 $\mu g\ g^{-1}$); which compared well with the known value of 37.2 $\mu g\ g^{-1}$.

X-ray powder diffraction (XRPD) was used to identify the chemical forms of cadmium in the ash of some of the plastics. For each sample, some of the ash was mixed with alcohol (in a mortar, with a pestle). The solution was dabbed on a clean glass slide, and the alcohol left to evaporate, leaving a fine layer of ash covering the slide's surface. The calibration of the XRPD machine was checked against diffracted peaks of a standard silicon wafer, and samples (ash covered slides) were scanned for diffracted X-rays over the two-theta angular range 10-60° (usually). The step size was 0.05°, and the counting time at each step was 5 seconds.

X-ray diffractograms of samples were compared with those of cadmium sulphide (AR grade) and cadmium selenide. Cadmium selenide was prepared by heating a mixture containing 3.15 grams of cadmium oxide, 3.71 grams of cadmium sulphide and 6 grams of selenium in a covered quartz crucible for 15 minutes at 800 °C (following the recipe recommended by Brauer (1963)). Further details of the XRPD technique are given in Chapter 14.

An assessment was made of how readily cadmium would be likely to leach from some of the cadmium-pigmented plastics in the human stomach. Most of the time, hydrochloric acid in the human stomach is at pH 1–2 (Davenport, 1966). Each plastic item was placed in 50 ml of 1.5 M hydrochloric acid (AR) in a 250 ml conical flask, which was then covered and left in a water-bath at 37 °C (human body temperature) for 24 hr and 48 hr. The conical flasks were occasionally agitated. The leachates were analysed by GFAAS. Analytical parameters used were the same as those given in section 3·2·2 and Chapter 14 for the GFAAS analysis of cadmium.

One sauce container (which was known to be coloured with a cadmium pigment) was subjected to the leaching method prescribed for "...vessels not used for cooking" in the New Zealand Food and Drug Regulations (Anon. 1973). This involved the following steps:
1. washing of the interior of the vessel with water containing some detergent;

2. removal of "all traces of" detergent by washing the vessel's interior with the leaching solution—4% acetic acid;
3. filling the vessel with leaching solution, covering the top, and leaving it at room temperature for 24 hr;
4. thorough stirring of the solution before analysis.

AR grade acetic acid (diluted with double-distilled water) was used for this part of the study. Once again, GFAAS was used to analyse the leachate.

5·3 Results and discussion

5·3·1 Concentrations of cadmium

Experimentally determined concentrations of cadmium in 102 items analysed are given in Table 5·1.

Table 5·1

Concentrations of cadmium in commercial products.

Item	Colour (if applicable)	Number of analyses	Cadmium concentration ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	95% error on mean[a] ($\mu g\ g^{-1}$)
Alloys					
"Alutin" solder		4	15 000	100	±130
Ceramic glazes	Red	4	4 390[b]	820	±1 100
	Yellow	1	<0.3		
Crayons	Blue	1	<0.2		
	Red	1	<0.2		
	Yellow	1	<0.2		
Dyes	Orange	1	<0.1		
	Red	1	<0.1		
	Yellow	1	<0.1		
Dyed wool	Orange	3	<0.4		
Inks Printers' ink	Red	4	5.43[b]	2.89	±3.92
Pages from magazine	Red	2	<0.1		
Paints[c]					
Artists' paint[d]	Yellow	4	235 000	5 600	±6 000
Childrens' paints Brand # 1[d]					
	Lemon-yellow	4	11.2	0.8	±1.1
	Pale orange	1	<0.04		
	Vermillion	1	<0.03		
	Yellow	1	<0.04		
	Yellow-ochre	1	<0.03		

Table 5·1 continued...

Item	Colour (if applicable)	Number of analyses	Cadmium concentration ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	95% error on mean[a] ($\mu g\ g^{-1}$)
Brand # 2[d]					
	Crimson	1	<0.03		
	Gamboge tint	1	<0.05		
	Lemon-yellow	1	<0.03		
	Vermillion	1	<0.04		
	Yellow-ochre	1	<0.06		
Brand # 3[e]					
	Red	2	4.42	2.67	±16.8
	White	1	<0.5		
	Yellow	2	5.95	2.09	±13.2
Spray-paint	Red	5	31 300	2 300	±2 400
Paint scraped from...					
Pencil	Red	2	<0.3		
	Yellow	1	<0.3		
Tomato sauce can	Red	1	<3		
Soft-drink can	Red	1	<5		
Plastics					
Ball-point pen					
Body	Yellow	1	2 530		
"Clicker"	Red	2	1 450	672	±4 200
Basket	Red	1	584		
Bowl					
Brand # 1	Red	1	<0.2		
Brand # 2	Red	4	5.03	2.90	±3.93
Bread-bag	Red	1	<0.5		
Brush and pan set	Yellow	1	2 790		
Bucket	Red	1	879		
Cassette case	Yellow	1	<0.4		
Childrens' building-blocks					
Brand # 1	Red	1	1.46		
Brand # 2	Red	1	6 680		
	White	1	14.4		
	Yellow	1	11 100		
Childrens' beads	Green	1	<2.5		
	Orange	1	<2.2		
	Pink	1	<2.6		
	Purple	1	<2.1		
	Red	1	<2.1		
	White	1	<0.6		
	Yellow	1	<2.2		

Table 5·1 continued...

Item	Colour (if applicable)	Number of analyses	Cadmium concentration ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	95% error on mean[a] ($\mu g\ g^{-1}$)
Clothes-peg	Blue	1	0.950		
	Orange	1	2.18		
	Red	1	3 330		
	Yellow	1	1 270		
Coathanger	Red	1	<0.4		
Coffee-jar lid	Brown	1	<0.2		
Cup					
Brand # 1	Red	1	<2.4		
Brand # 2	Red	1	<2.2		
Detergent bottle-tops					
Brand # 1	Yellow	1	824		
Brand # 2	Red	1	2 600		
Brand # 3	Red	1	1 600		
Dish-scrubber handle	Yellow	2	2 280	35.4	±220
Disposable razor	Yellow	1	2.94		
Dog dish	Red	1	3 050		
Felt-pen body					
Brand # 1	Red	1	1 070		
	Yellow	1	1 140		
Brand # 2	Blue	1	5.10		
	Orange	1	384		
	Yellow	1	1 190		
Fish-slice	Red	3	<0.9		
Flask	Yellow		<0.5		
Lemonade container	(Clear)	1	<0.4		
Lemon-juice container	Yellow	3	10.9	0.36	±0.74
Lunchbox	Red	3	<1.5		
Oil container	Red	1	0.985		
Peanut-oil container top	Yellow	1	64.0		
Plate	Red	3	3 710	165	±340
Removable bolt from a mop	Yellow	1	3 330		

Table 5·1 continued...

Item	Colour (if applicable)	Number of analyses	Cadmium concentration ($\mu g\ g^{-1}$)	Standard deviation ($\mu g\ g^{-1}$)	95% error on mean[a] ($\mu g\ g^{-1}$)
Sauce containers					
Soy sauce	Red	1	6.13		
Tobasco sauce	Red	4	265	8	±11
Steak sauce	Red	6	2 940	60	±50
Sauce dispenser	Red	4	2 450	101	±140
Shaving-foam container top	Red	1	2 470		
Stapler	Orange	1	3 290		
Stock pot body	Yellow	1	2 680		
Stock pot lid	Red	1	3 670		
Toothbrush					
Brand # 1	Red	1	38.8		
Brand # 2	Yellow	1	919		
Toy duck	Yellow	1	<0.5		
Toy lion	Red	1	1 410		
Turpentine bottle	(Clear)	1	<0.8		
lid	Red	1	2 060		
"Vegemite" jar lid	Yellow	2	1 570	113	±696
Volumetric flask top	(Clear)	1	<0.3		
	Red	2	558	134	±844
	Yellow	2	864	349	±2 200
Rubber and synthetic rubber					
Balloon	Yellow	1	0.574		
Gloves	Yellow	1	0.995		
Vacuum tubing	Red	1	0.072		
Miscellaneous items					
Coke		2	0.159	0.026	±0.165
Liquid pot-plant fertilizer		1	11.3		
Superphosphate fertilizer		5	8.97	0.38	±0.28

Notes: **a.** Student's t-test.
b. Wet weight.
c. Wet weight except for Brand # 3.
d. Water-based.
e. Oil-based.

Analytical precision can be estimated from the data in Table 5·1. The mean coefficient of variation (100 x standard deviation/mean) of the 21 samples analysed more than once is 19.0%. However, there is a wide spread in the values of the coefficients of variation between samples—from 0.6% for the cadmium-containing solder ("Alutin") to 60% in the case of the red childrens' paint (Brand # 3). In the latter case, the heterogeneity of the paint could contribute to the poor precision.

The highest concentration of cadmium is 23.5% (wet weight) in the water-based "cadmium-yellow" artists' paint. Assuming all the cadmium was present as the sulphide form (XRPD analysis below tended to confirm this), the paint would be 30.2% cadmium sulphide. No warning of toxicity was given on the label of this tube of paint. Based on the paint's cadmium content, an artist resolved on a particularly poignant means of earthly departure would have to ingest between 1.49 and 38.3 g (using the toxicity figures of Yasumura *et al.* (1980) given in section 1·4·3).

At the time of this study, a 7.5 ml tube of "cadmium-yellow" artists' paint cost N.Z. $5.80, and could only be purchased from retailers who specialized in selling artists' supplies. These factors effectively make the paint less accessible to children (the group most likely to ingest paint). Artists would be best advised not to lick their brushes.

One of the water-soluble childrens' paints (Brand # 1, lemon yellow) contains 11.2 μgCd g^{-1} (wet weight) (Table 5·1). Although this concentration is comparatively low, in the view of the author it is insufficiently low to justify the use of the words "non-toxic" on the lid of the paint box.

A heat-resistant variety of red spray-paint (used for such applications as painting cars) is about 3% cadmium (dry weight). Experiments involving the leaching of cadmium from a surface finished with this paint are detailed in Chapter 13.

On the bottle of the red ceramic glaze which contains 4 390 μgCd g^{-1} (wet weight) (Table 5·1) a clear warning is printed which specifies that the glaze is not to be used "...on surfaces that may come into contact with food or drink." (The dry weight cadmium concentration of the glaze would be substantially higher than the wet weight concentration.)

Almost half (32 of 66) of the plastics studied have cadmium concentrations in excess of 500 μg g^{-1} (Table 5·1). All of these are coloured either red (n = 18), orange (n = 1) or yellow (n = 13), suggesting that cadmium-compounds have been used in the plastics as colouring agents (rather than as stabilizers). (This subject is examined further in section 5·3·2.) The mean concentration of cadmium in these plastics is 2 390 μg g^{-1} (with a standard deviation of 2 050 μg g^{-1}). Cadmium concentrations in small (less than about 1.25 cm^3) swallowable childrens' toys range from below the detection limit (*e.g.* childrens' bead set) to 11 100 μg g^{-1} (yellow building-block, Brand # 2). Leaching of cadmium under simulated stomach conditions from plastic items is discussed further in section 5·3·3. Ball-point pens and felt pens, some of which have high concentrations of cadmium, are often sucked. Similarly, one of the toothbrushes (the yellow one) contains 919 μgCd g^{-1} (Table 5·1).

Substantial amounts of cadmium are also associated with the red and yellow plastic tops of volumetric-flasks (Table 5·1). This could cause contamination problems during the acid washing of glassware. Throughout this project, (clear) polypropylene or glass volumetric-flask tops were used (Chapter 14).

High concentrations of cadmium are present in the plastic of some of the food containers (Table 5·1). Surprisingly, among these are vessels of acidic foods: a red plastic steak-sauce container (2 940 $\mu gCd\ g^{-1}$), a tobasco-sauce bottle (265 $\mu gCd\ g^{-1}$) and a tomato-shaped sauce dispenser (2 450 $\mu gCd\ g^{-1}$). The pH of the steak-sauce was 3.15, and that of the tobasco-sauce was 2.90; both sauces therefore being thermodynamically favourable media for the formation of the Cd^{2+} ion (section 1·3·2; Hermann and Neumann-Mahlkau, 1985). This subject is further examined in section 5·3·3. However, it is worthy of note that because of the high toxicity of cadmium, the use of cadmium-based stabilizers in plastic containers that come into contact with food is prohibited in the U.S.A. (Hollander and Parker, 1978).

Cadmium and zinc concentrations in the rubber of six different brands of car tyres are given in Table 5·2.

Table 5·2

Cadmium and zinc contents of the rubber from six brands of car tyres, and the mean concentrations of cadmium and zinc in background soil samples[a].

	Concentration of cadmium ($\mu g\ g^{-1}$)	Concentration of zinc ($\mu g\ g^{-1}$)	% of cadmium in the zinc[b]
Tyres			
Brand # 1	0.409	721	0.05
Brand # 2	1.37	1 760	0.08
Brand # 3	0.514	1 420	0.04
Brand # 4	0.806	1 760	0.05
Brand # 5	0.269	2 140	0.01
Brand # 6	0.240	1 230	0.02
Mean	0.601	1 230	0.04
Std. deviation	0.429	496	0.02
Error on mean[c]	±0.432	±500	±0.02
Background soil[a]			
Mean	0.104	53.2	
Std. deviation	0.047	4.1	
Error on mean[c]	±0.097	±8.5	

Notes: **a.** Mean of the three background values given in Table 3·6.
b. Assuming that all the cadmium is associated with zinc.
c. Student's t-test error on mean at a 95% confidence level.

The data in Table 5·2 imply that abrasion of rubber fragments from car tyres would cause enrichments of cadmium and zinc in road-dust. Car tyre rubber has about 6 times more cadmium, and 28 times more zinc, than background soil. Previous researchers have identified the existence of a correlation between traffic densities and road-dust cadmium

concentrations (section 2·1·2c). Abrasion of car tyres is likely to contribute to this relationship. The absolute concentrations of cadmium in some of the car tyres (Brands 1, 5 and 6) are not very high, and it is interesting to note that rubber fragments worn from these tyres would have the effect of *reducing* the cadmium concentration in some roadside dusts (by comparison of the data in Table 5·2 with that in Table 3·7).

5·3·2 Speciations of cadmium in plastics

The X-ray powder diffraction patterns of cadmium sulphide, cadmium selenide, the artists' paint, and the ash of eight red and yellow plastic items are given in Figure 5·1 (pages 126–131).

The distances between parallel sets of lattice planes (or "d-spacings") in Ångströms and the relative peak intensities of cadmium sulphide and cadmium selenide found in this study compare well with tabulated values (Appendix 5·1).

The XRPD pattern of cadmium sulphide is very similar in shape to that of cadmium selenide (Figure 5·1). This is because the two compounds are isomorphous—both have hexagonal unit cells (Smith, 1967, file numbers 6-314 and 8-459). The d-spacings of each cadmium selenide peak are larger than those of corresponding cadmium sulphide peaks (*i.e.* the dimensions of the unit cell are larger for cadmium selenide than they are for cadmium sulphide) because selenium has a larger ionic radius (1.91 Å) than sulphur (1.84 Å) (Weast and Astle, 1983).

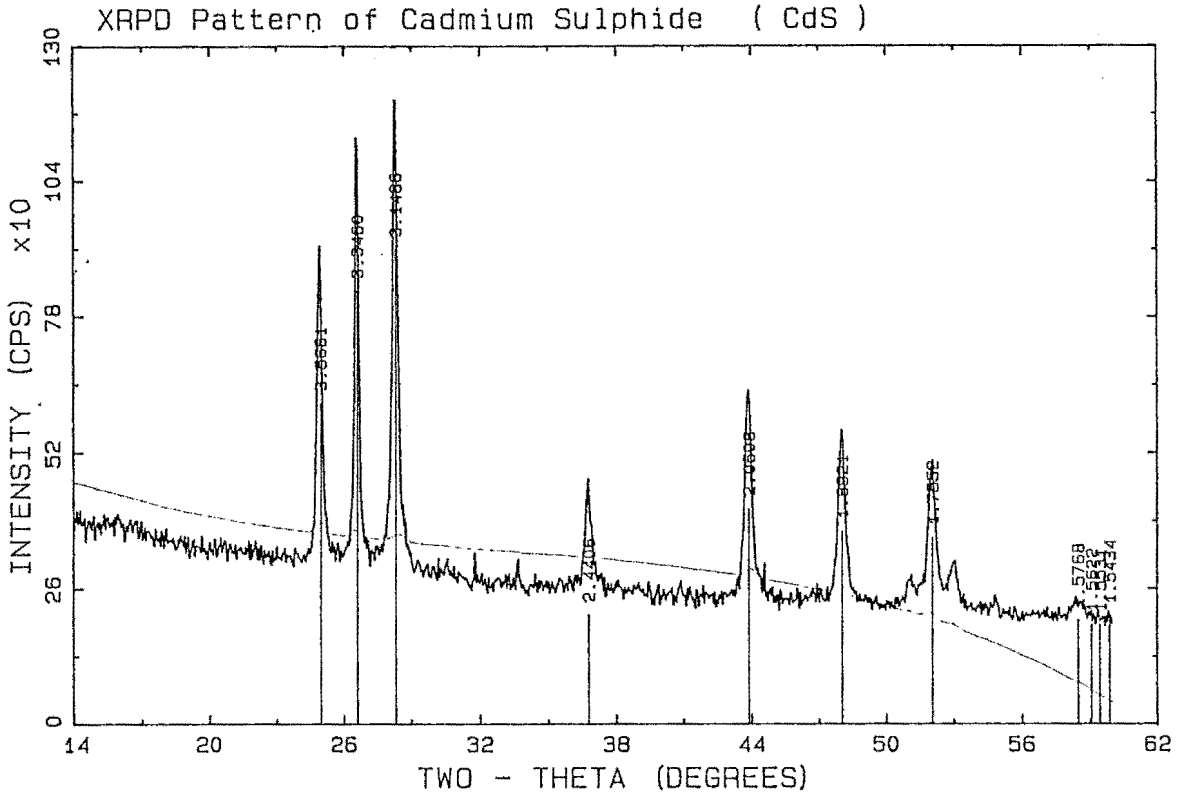
The pattern of cadmium sulphide is readily identifiable in the XRPD patterns of the artists' (yellow) paint and the yellow ball-point pen ash (Figure 5·1). XRPD patterns of the ashes from the yellow dish-scrubber handle, yellow "beef-stock" container and yellow "vegemite" jar lid are more complicated, and show peaks corresponding both with cadmium sulphide and barium sulphate. The first eight d-spacings (in Å) and their relative intensities (as subscripts) of barium sulphate given in the literature are 3.44_{10}, 3.10_{10}, 2.12_{8}, 2.10_{8}, 3.32_{7}, 3.90_{6}, 2.83_{5} and 2.73_{5} (Berry, 1972). Peaks of barium sulphate are most obvious (and peaks of cadmium sulphide are most obscured) in the XRPD pattern of the ash from the "vegemite" jar lid (Figure 5·1). Barium sulphate (also known as *blanc fixe*) is widely used industrially as a filler in plastics and as a white pigment (Baudis *et al.* 1985). Because of its low solubility (2×10^{-4} wt% at 20 °C), barium sulphate is regarded as non-toxic.

Thus, the chemical form of cadmium used to colour plastics yellow is (in the plastics studied) cadmium sulphide (CdS).

Cadmium sulphide can be oxidized in air (in the presence of some moisture) to cadmium sulphate ($CdSO_4$) and hydrated sulphates ($CdSO_4.H_2O$ and $3CdSO_4.8H_2O$) and then to cadmium oxide (CdO) by heating from 300–700 °C (Hollander and Parker, 1978). However, XRPD patterns attributable to these species were not observed (Figure 5·1), implying that the yellow pigment cadmium sulphide was stable under the ashing conditions used. One reason that cadmium sulphide and cadmium thioselenide are used as pigments is that they are heat stable to 600 °C (Nriagu, 1980).

Figure 5·1

X-Ray diffraction patterns of cadmium sulphide, cadmium selenide, "cadmium yellow" artists' paint and the ash of eight red and yellow plastic items. Numbers printed on peaks are "d-spacings" (spacings between parallel sets of lattice planes) in Ångströms.



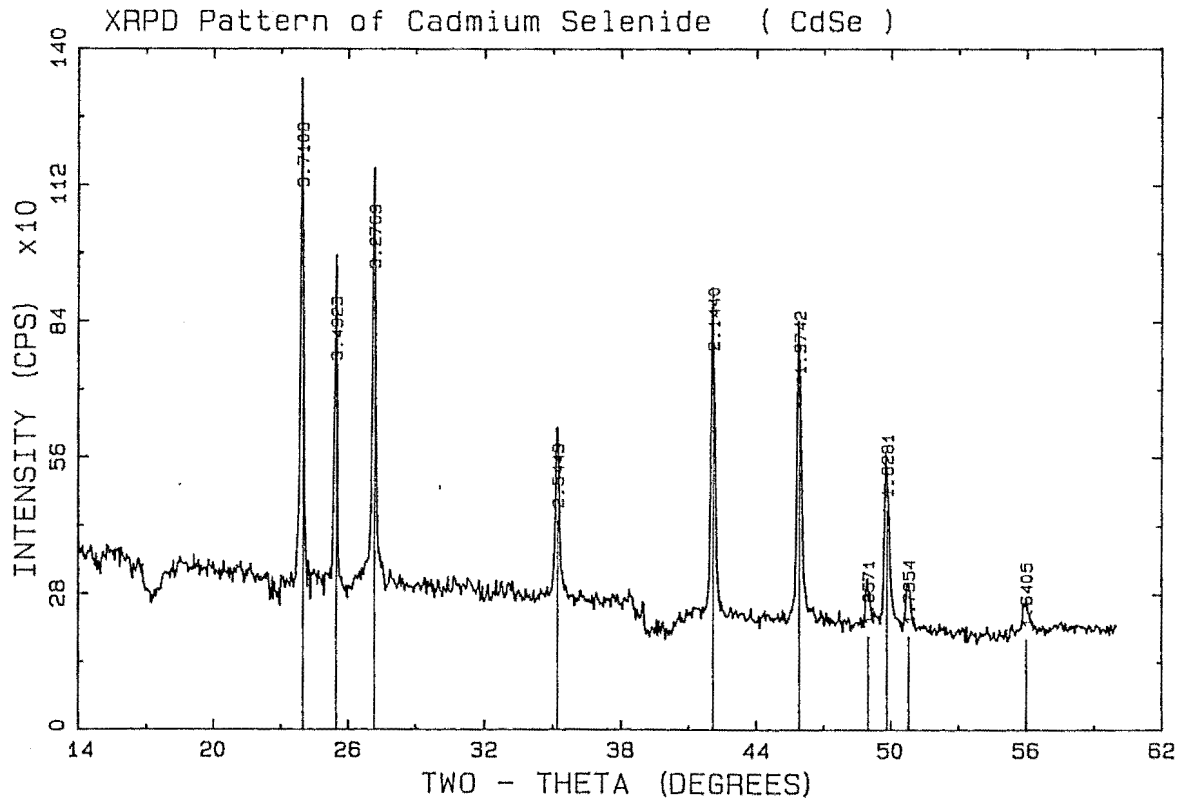
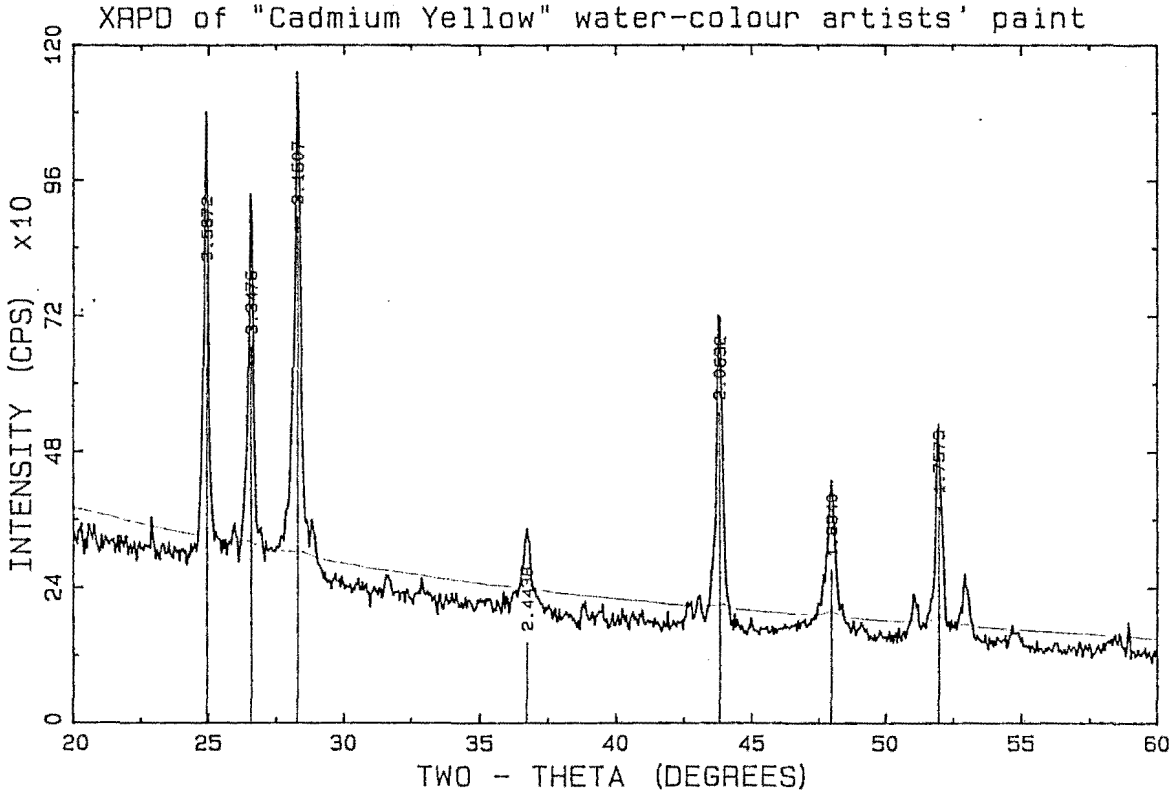
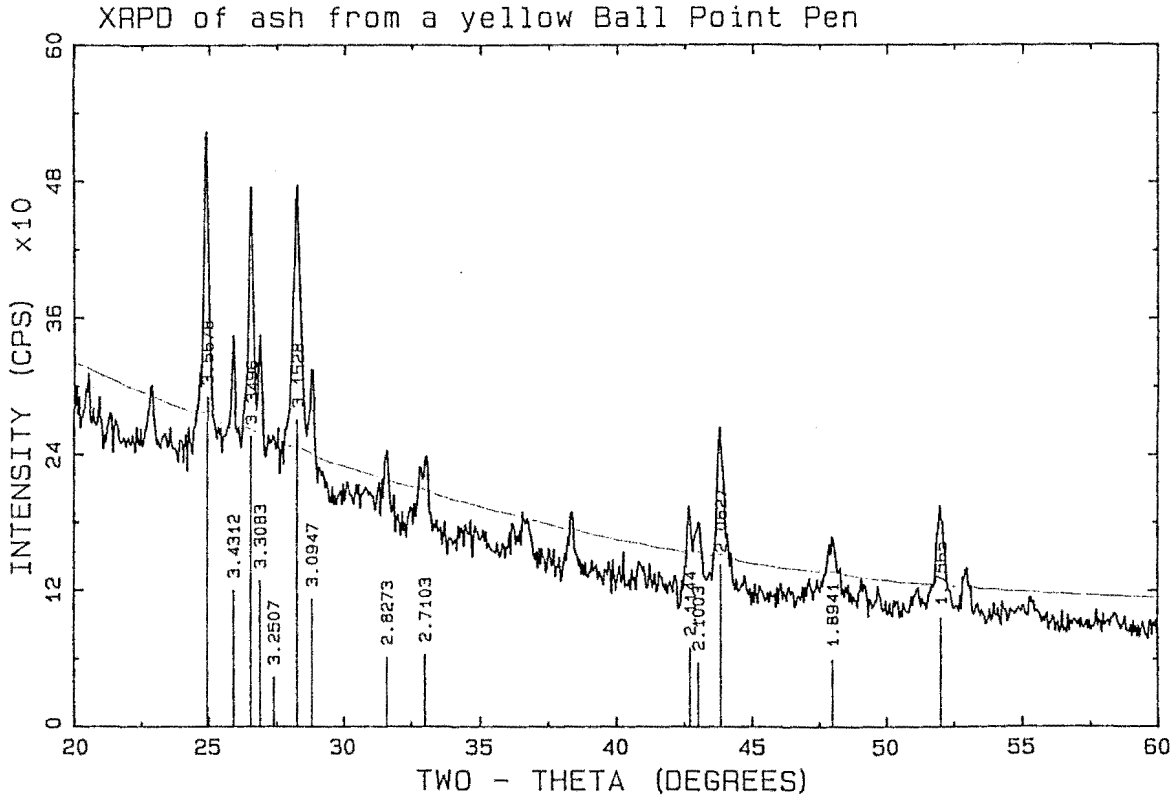


Figure 5·1 continued...





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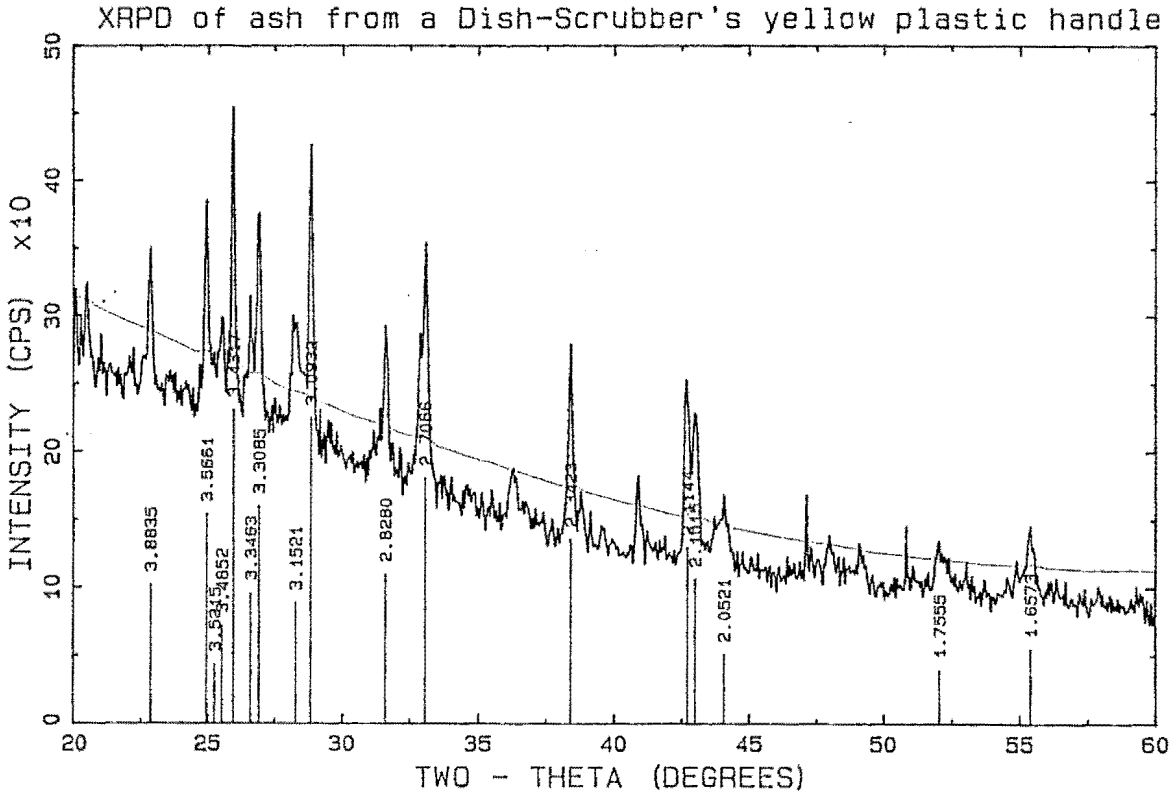

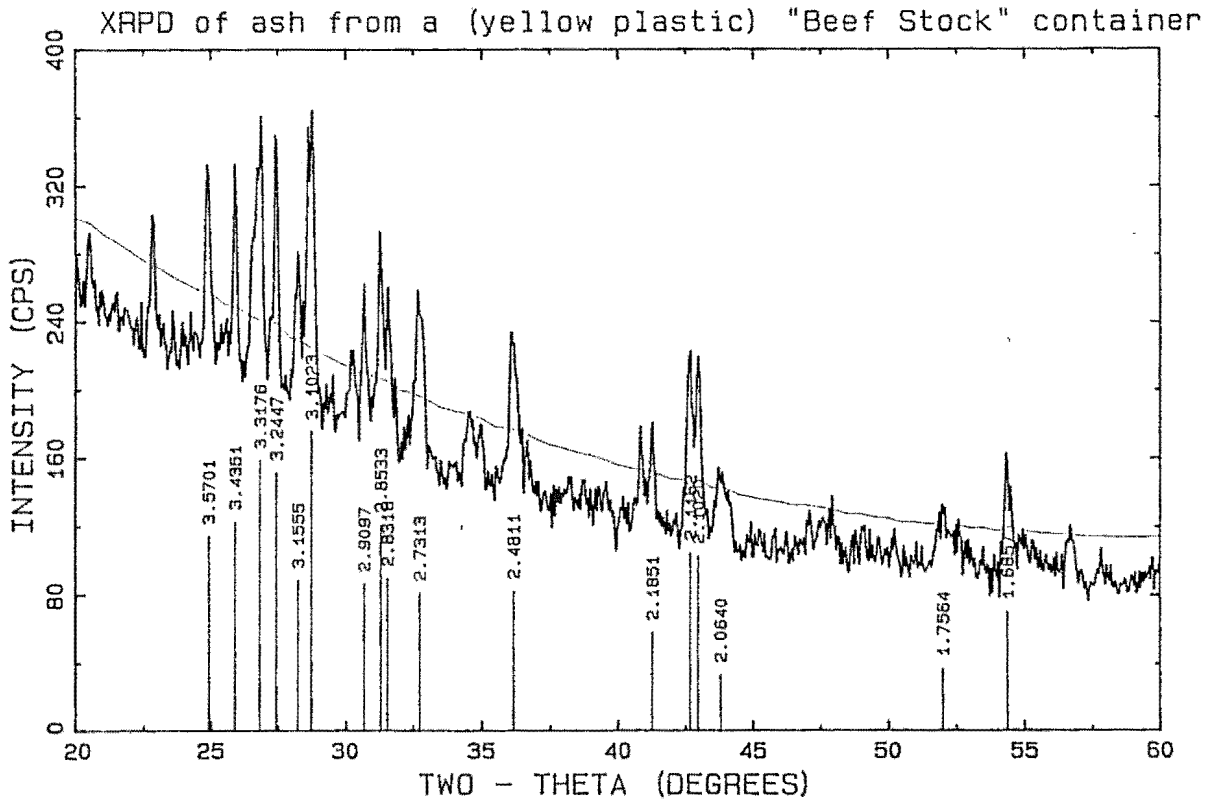

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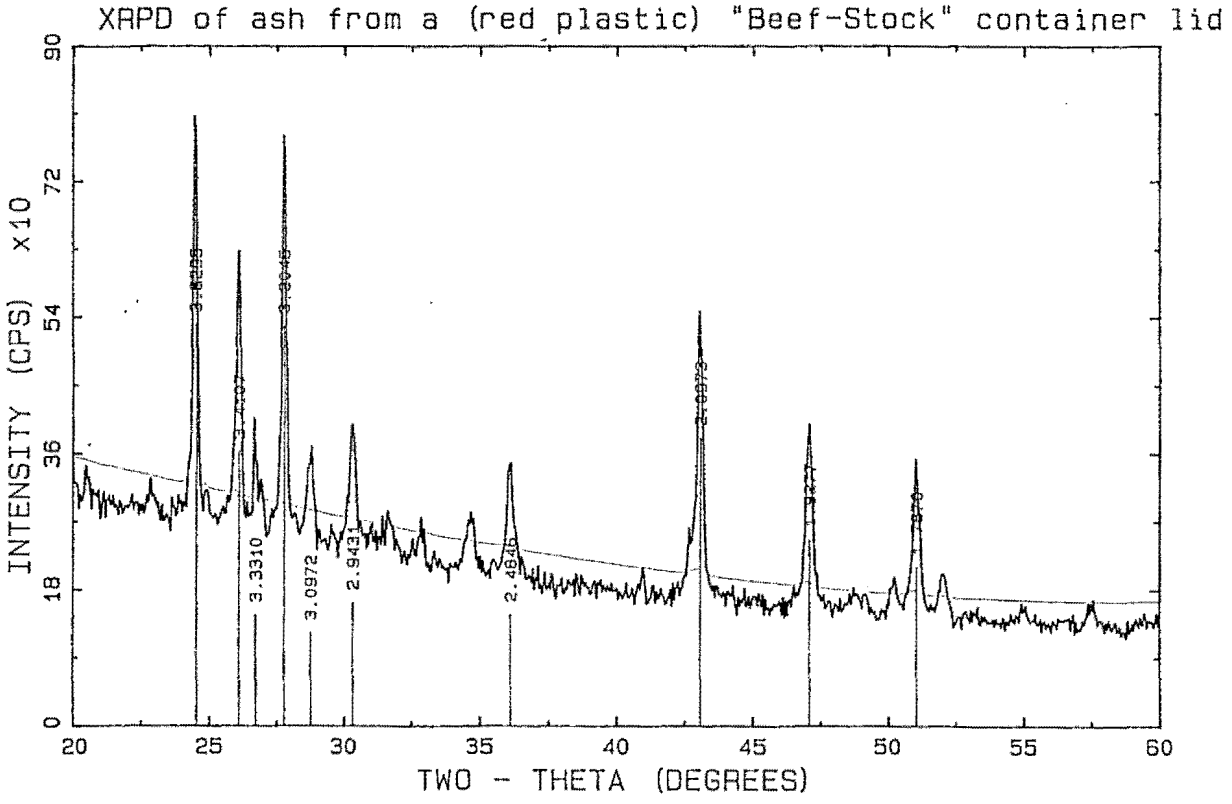


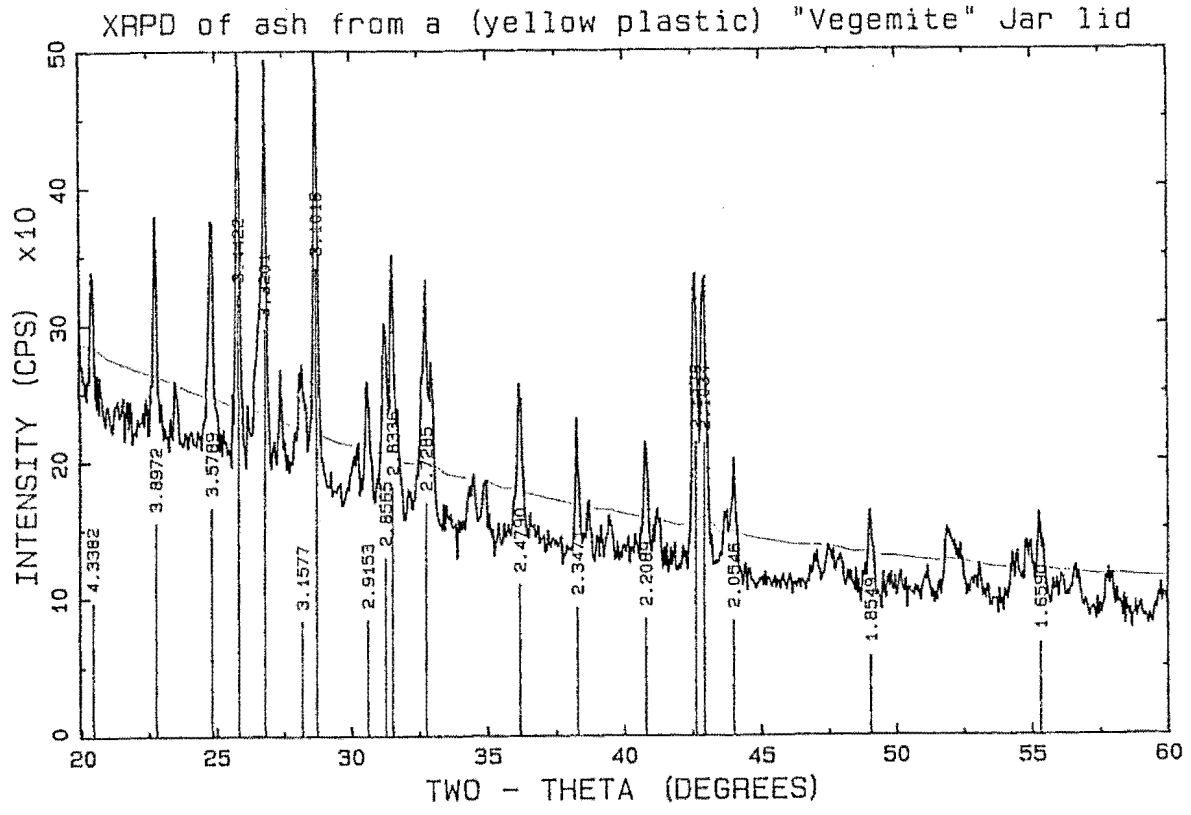
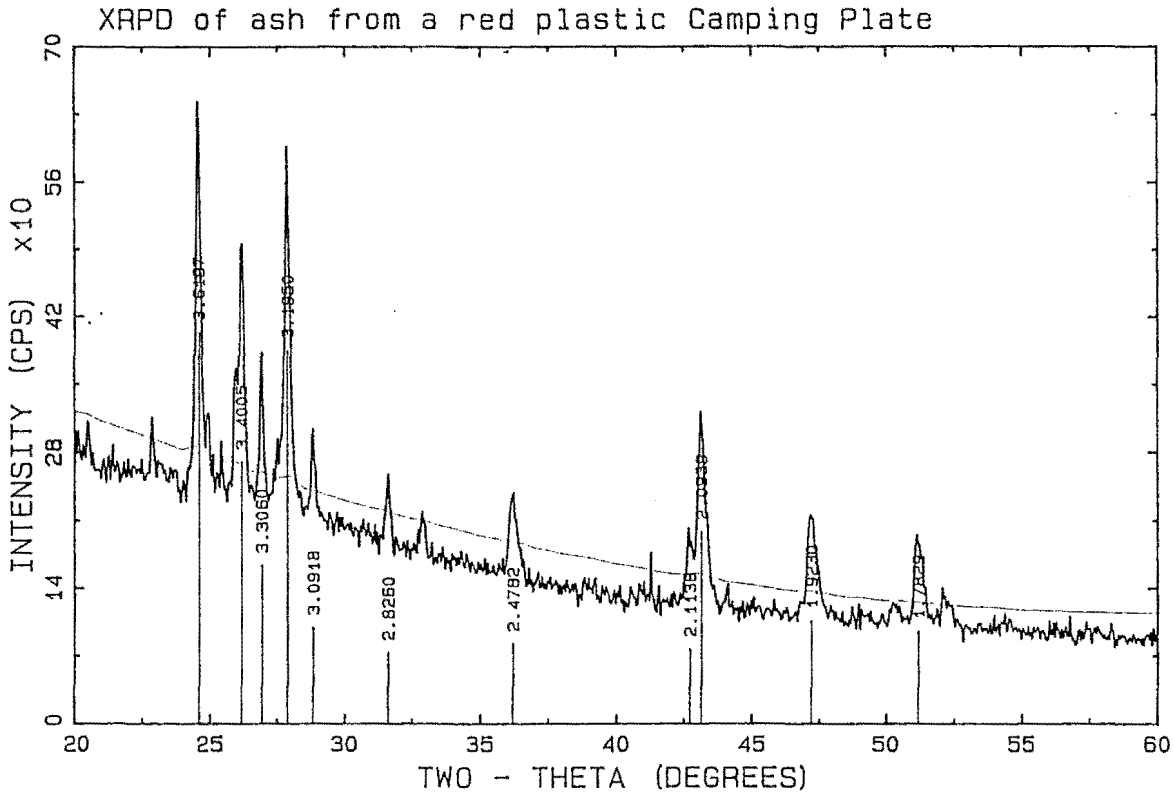


Figure 5·1 continued...



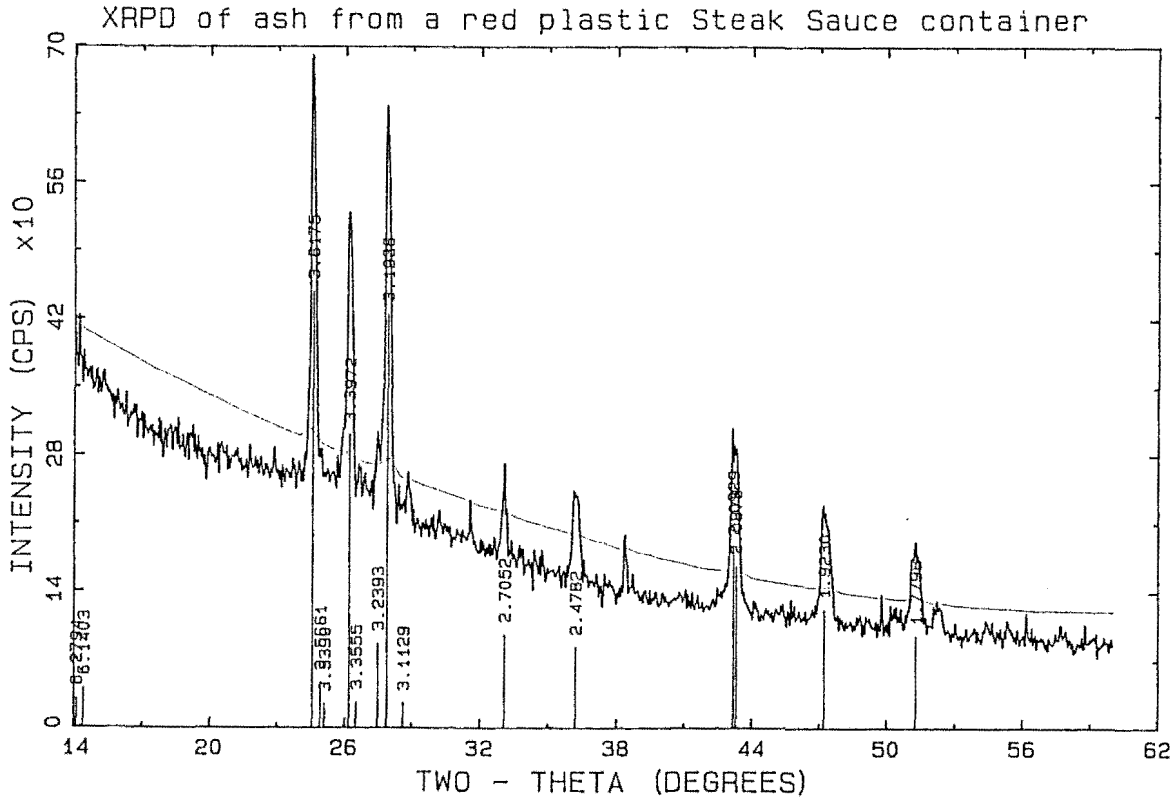
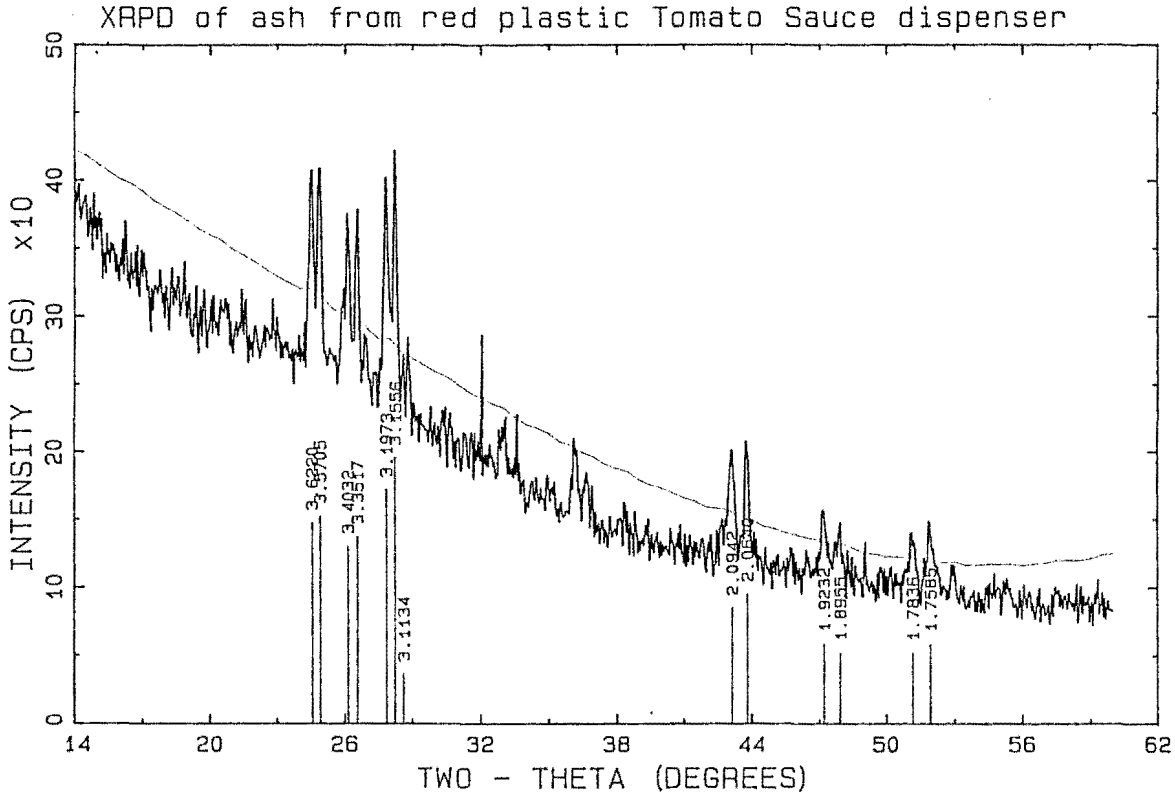


Figure 5·1 continued...



Ashes of red plastic items have XRPD patterns of the same general shape as those of cadmium sulphide and cadmium selenide (Figure 5·1). However, each peak of the XRPD patterns of the red plastic items is at a d-spacing which falls somewhere between the d-spacings of that peak for cadmium sulphide and cadmium selenide. For example, whereas the largest d-spacing of cadmium sulphide is 3.57 Å and that of cadmium selenide is 3.71 Å, the largest d-spacing of the ash from the red plastic camping-plate is 3.62 Å. Furthermore, FAAS analysis of seven red and yellow plastic items revealed that selenium was present in the red plastics, but not at the levels required for a 1:1 molar ratio of selenium with cadmium (Table 5·3).

Table 5·3

Cadmium and selenium content of some red and yellow plastic items.

	μgCd g^{-1} **a**	μgSe g^{-1}	μmoleCd g^{-1}	μmoleSe g^{-1}
Red plastics				
Plate	3 710	879	33.0	11.1
Sauce-dispenser	2 450	269	21.8	3.41
Steak-sauce container	2 940	506	26.2	6.41
Volumetric-flask top	558	162	4.96	2.05
Yellow plastics				
Dish-scrubber handle	2 280	<2	20.3	<0.03
"Vegemite" jar lid	1 570	<7	14.0	<0.09
Volumetric-flask top	864	<2	7.69	<0.03

Note: **a.** From Table 5·1.

The species of cadmium in the red plastic items investigated is likely to be the thioselenide, a solid solution of cadmium, sulphur and selenium of general formula $CdS_xSe_{(1-x)}$. The XRPD pattern of the species $CdS_{0.9}Se_{0.1}$ would be nearest in d-spacings to the pattern of cadmium sulphide, whereas the XRPD pattern of $CdS_{0.1}Se_{0.9}$ would resemble that of cadmium selenide more closely (the unit cell would expand as more selenium is substituted for sulphur).

The XRPD pattern of the tomato-sauce dispenser ash (Figure 5·1) serves as a confirmation that small shifts in d-spacings are due to different cadmium species (and not to dissimilarities between experimental runs). Twin sets of peaks appear throughout the pattern. D-spacings of the peaks on the right side of each pair resemble those of the cadmium sulphide pattern most closely ; d-spacings of the peaks on the left side of each pair are closer to those of the other red plastic items.

Estimates of the molar compositions of the cadmium thioselenides can be made from the XRPD patterns by assuming that enlargement of the unit cell upon substitution of selenium for sulphur is a linear process (which is not necessarily true). Molar compositions of cadmium thioselenides determined by this method are listed alongside those calculated from the results of the FAAS analysis in Table 5·4.

Table 5·4

Estimates of the molar composition of cadmium thioselenides associated with red plastic items.

Item involved	Method upon which estimate is based	
	FAAS[a]	XRPD
"Beef stock" container		$CdS_{0.54}Se_{0.46}$
Plate	$CdS_{0.66}Se_{0.34}$	$CdS_{0.60}Se_{0.40}$
Steak-sauce container	$CdS_{0.76}Se_{0.24}$	$CdS_{0.66}Se_{0.34}$
Tomato-sauce dispenser[b]		$CdS_{0.84}Se_{0.16}$
Volumetric-flask top	$CdS_{0.59}Se_{0.41}$	

Notes: **a.** Calculated from the data in Table 5·3.
b. An estimate based on FAAS analysis cannot be made in this case, as it is unknown how much of the cadmium is present as cadmium sulphide.

In the two cases where estimates were made based on both methods (FAAS and XRPD) agreement is reasonable. The most popular cadmium thioselenide appears to be the one approximated by the formula $CdS_{0.6}Se_{0.4}$.

5·3·3 Leaching of cadmium from plastics

The results of the experiment to assess the extent of leaching of cadmium from plastics coloured with its compounds under "simulated stomach conditions" (1.5 M HCl at 37 °C) are given in Table 5·5. The amount of cadmium leached would depend on the surface-area of plastic exposed to acid, the cadmium content and porosity of the plastic, and the kinetic and thermodynamic stabilities of exposed cadmium sulphide and thioselenide species under acidic conditions.

Two conclusions can be made from the data in Table 5·5:

1. Very little cadmium is liberated from the plastics under these conditions. Overall, the mean amount of cadmium leached represents only about 0.13% of the cadmium content of the plastics. More cadmium than this would probably be released in a human stomach, due to the effects of enzymatic action on the plastics. However, it should also be remembered that only about 6% of ingested cadmium is absorbed (section 1·4·2).
2. In all cases, most or all of the leached cadmium was liberated within the first 24 hr period. This suggests that the amount of leachable cadmium is limited, and is governed by the amount available to acid on the surfaces of the plastics.

Table 5·5

The amount of cadmium leached from six cadmium-containing plastics under "simulated stomach conditions".

Item	Dimensions (mm)	Cadmium content[a] (μg g^{-1})	μgCd leached in 50 ml		μgCd leached g^{-1}[b]	
			After 24 hr	After 48 hr	After 24 hr	After 48 hr
Red plastics						
Childrens' building block	32 x 16 x 12	6 680	1.50	1.50	0.58	0.58
Plate	15 x 15 x 2[c]	3 710	1.04	0.90	0.63	0.54
Tomato-sauce dispenser	10 x 10 x 2[d]	2 450	0.50	0.50	0.22	0.22
Yellow plastics						
Childrens' building block	32 x 16 x 12	11 100	4.20	6.40	1.64	2.49
Ball-point pen	10 x 5 x 1[d]	2 530	40.0	59.2	13.3	19.7
Peg	72 x 18 x 5	1 270	0.44	0.45	0.22	0.22

Notes: **a.** From Table 5·1.
b. μg of cadmium leached per gram of plastic.
c. Five pieces.
d. Eight pieces.

The (2 940 μgCd g^{-1}) red plastic steak-sauce container was subjected to the leaching method outlined in the New Zealand Food and Drug Regulations (Anon. 1973) for testing the cadmium leachable from vessels not used for cooking. (Under these regulations, leachable cadmium should not exceed 0.7 μg ml^{-1}.) No cadmium was detected in the leachate (4% acetic acid) after 24 hr—concentrations were below the GFAAS detection limit (0.15 μg l^{-1}). There were two possible reasons for this: either the cadmium thioselenide pigment was stable to 4% acetic acid for 24 hr, or the leachable cadmium had already been incorporated into the steak-sauce (pH 3.15). If the latter explanation is true, the actual amount of leachable cadmium appears to be low. The mean cadmium concentration of seven samples of the steak-sauce was 0.0065 μg g^{-1} (wet weight) (standard deviation 0.0044 μg g^{-1}). The maximum allowable limit given in the New Zealand Food Regulations is 1 μgCd g^{-1} (Anon. 1984).

In summary, it seems that cadmium-pigmented plastics would not pose a significant hazard to health if swallowed (provided the plastic is not broken down in the stomach by enzymes), and do not contribute large amounts of cadmium to food when used as food containers.

One potential problem (in health terms) not considered here is the ultimate disposal of cadmium-pigmented products by incineration. This makes a significant contribution to the direct respiratory intake of cadmium in humans (Piotrowski and Coleman, 1980).

5·4 Conclusion

Concentrations of cadmium were measured in 108 commercial products. "Cadmium-yellow" water-based artists' paint (30.2% CdS) was the most potentially lethal of these; in terms of the cadmium content, ingestion of between 1.5 and 39 g of this paint would be sufficient to kill an adult.

About half of the plastic items studied had cadmium concentrations exceeding 500 $\mu g\ g^{-1}$; cadmium was associated with red (cadmium thioselenide) and yellow (cadmium sulphide) pigments in these plastics.

Several "high-cadmium" plastics were either small and swallowable, or were food containers. A small amount of cadmium (about 0.13% of that available) was leached from red and yellow plastic items under conditions designed to approximate those found in the human stomach. Surface interactions appeared to be the limiting factor governing the amount of cadmium leachable from plastics. Overall, it was thought unlikely that ingestion of a plastic item pigmented with cadmium would lead to acute cadmium poisoning. No (or very little) cadmium was liberated by 4% acetic acid in 24 hr from the interior of a cadmium thioselenide-pigmented steak-sauce container.

The cadmium and zinc content of car tyres were found to be 6 and 28 times higher (respectively) than mean concentrations of these metals in background soils. Abrasion of car tyres is likely to be a source of both metals in roadside dusts; however, rubber fragments of some brands of tyres would actually serve to *dilute* cadmium concentrations in some road-dusts.

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5·6 Appendix

Appendix 5·1 (section 5·3·2)

Literature values[a] and values obtained in this study of the d-spacings (Å) and relative intensities of the XRPD patterns of cadmium sulphide and cadmium selenide.

Compound	Literature values		Values obtained in this study	
	D (Å)	Rel. intensity	D (Å)	Rel. intensity
CdS	3.58	75	3.57	66
	3.36	60	3.35	90
	3.16	100	3.15	100
	2.45	25	2.44	22
	2.07	55	2.06	45
	1.90	40	1.89	36
	1.76	45	1.75	32
CdSe	3.72	100	3.71	100
	3.51	70	3.49	65
	3.29	75	3.28	82
	2.55	35	2.54	34
	2.15	85	2.14	64
	1.98	70	1.97	60
	1.86	12	1.86	10
	1.83	50	1.83	33
	1.80	12	1.80	9
	1.65	8	1.64	5

Note : **a.** Smith, 1967.

CHAPTER 6
A SURVEY OF CADMIUM, COPPER AND ZINC CONCENTRATIONS IN FOODS

6·1 Introduction

Food accounts for over 90% of the body burden of cadmium in non-smokers who are not occupationally exposed to cadmium or its compounds (section 1·4·2).

The results of previous surveys relating to cadmium levels in New Zealand foods are discussed in section 2·2. In the most recently published survey (Pickston *et al.* 1985), the estimated daily cadmium intake was significantly higher than previous estimates (Guthrie and Robinson, 1977 and 1978; Dick *et al.* 1978) (section 2·2·1).

The aims of this study were as follows:

1. to gather sufficient data for an estimate of the daily cadmium intake of Christchurch residents in 1989;
2. to identify which food groups are likely to contribute the most cadmium to the daily dietary intake of Christchurch residents;
3. to identify which of these foods also contain high concentrations of copper and zinc—two metals which can reduce dietary absorption of cadmium (Spivey-Fox, 1988; section 1·4·3).

6·2 Method

Most food samples were purchased at a large Christchurch supermarket on 9 June 1989. Beef liver and lamb kidney samples were bought at a nearby butchers' shop. Samples were chosen which were thought to represent a reasonable proportion of the normal diet, and usually fell into the following categories: cereal-based products, dairy products, drinks, fats and oils, fish, fruit, meat and poultry, sweet foods and vegetables. Tap and (cold) kettle-water samples were gathered in 250 ml (acid-washed and thrice double-distilled water rinsed) polypropylene bottles form the author's home and from associates' homes.

Perishable items (such as vegetables and eggs) were processed and analysed first. Breads and meats were deep-frozen until processing and analysis.

Samples were prepared as they would normally be for cooking or for eating uncooked; bananas, oranges, onions, potatoes and carrots were peeled; apples and pears were not peeled, and shells were discarded from eggs. In the case of cigarettes, the filters (but not the papers) were removed and discarded. Plastic disposable gloves were used when handling foods; these were renewed before handling each new item.

Fruits and vegetables were either chopped (with a stainless-steel knife) and mixed, or were homogenized in a blender. Most parts of the blender which were to come into contact with food were first soaked in 2 M AR nitric acid for 24 hr and rinsed several times with double-distilled water (DDW). Between samples the interior of the blender was thoroughly

rinsed with DDW. Meats and uncanned fish were thawed, passed through a mincer and homogenized. The mincer was washed only with DDW (not with acid) before use and between uses. No obvious signs of contamination of meat samples by cadmium, copper or zinc from the mincer were evident upon analysis.

Between 5 and 30 g of each sample (depending on the estimated moisture content and expected cadmium concentration) was weighed into a 100 ml pyrex beaker (previously acid and DDW washed) and ashed overnight at 450 °C in a muffle furnace. Oxygen was passed through the furnace to facilitate ashing. To avoid sputtering, some samples with high liquid contents (*e.g.* blended oranges, milk) were dried at 80–90 °C prior to ashing.

Water samples (200 ml) were frozen in clean 500 ml round-bottom flasks and freeze-dried (the freeze-drying technique is described more fully in Chapter 9). The residue was taken up in 5 ml of 4 M AR nitric acid and diluted to 10 ml.

Each ashed food sample was boiled in 15 ml of 4 M nitric acid for 30 minutes, left to cool and filtered through a (nitric acid and DDW washed) Whatman No. 540 filter paper. Residues were rinsed with DDW until the filtrate volume reached 25 ml (usually). Standards were prepared from 1 000 $\mu g\ ml^{-1}$ stock solutions and given the same acid strength as samples. Blanks comprised DDW-diluted AR nitric acid.

Solutions were analysed for copper and zinc by FAAS (parameters are given in Chapter 14). Solutions were analysed for cadmium by GFAAS with deuterium background correction. The GFAAS furnace heating program used in this study is given in Table 6·1.

Table 6·1

GFAAS furnace heating program for the measurement of cadmium in food extracts.

Step number	Step	Temperature (°C)	Ramp time (s)	Holding time (s)
1	Drying # 1	80	5	1
2	Drying # 2	120	4	1
3	Ashing	350	2	3
4	Atomization	2 000	1	1

Absorbance readings for cadmium were usually within the range 0.050–0.500. Cadmium absorption peaks were sharp and symmetrical, and the analytical limit of detection was usually about 0.2 $\mu g\ kg^{-1}$. (The limit of detection is taken here as the concentration corresponding to five times the standard deviation of the blank (Wilson, 1974).) At least two, and in most cases three samples of each food were analysed.

Samples of certified-reference hay (V-10, International Atomic Energy Agency, Vienna) were included with most batches of samples ashed and analysed. Hay was chosen because it was thought to be reasonably similar in composition to some of the food samples (particularly to cereal-based foods). The results of the replicate analyses of certified-reference hay are given in Table 6·2.

Table 6·2

Given and measured concentrations of cadmium, copper and zinc in certified-reference hay.

	Cadmium	Copper	Zinc
Certified values			
Concentration (μg g^{-1})	0.03	9.4	24
95% confidence interval	0.02–0.05	8.8–9.7	21–27
This study			
Number of analyses (n)	6	6	6
Mean concentration (μg g^{-1})	0.024	8.15	23.6
Standard deviation (μg g^{-1})	0.002	0.36	3.1
95% confidence interval[a]	0.022–0.026	7.83–8.47	20.8–26.4
Recovery[b] (%)	80	87	98

Notes: **a.** Student's t-test error on mean.
b. Taken here as 100[mean value obtained in this study/certified value].

The data in Table 6·2 indicate that there could be some loss of cadmium and copper during processing and/or analysis of standard reference hay. For cadmium this (possible) loss is not statistically significant, whereas for copper it is. Despite this, the estimated recovery of copper is still fairly high (87%).

6·3 Results and discussion

6·3·1 Concentrations of cadmium, copper and zinc in individual foods

Mean wet weight concentrations (and standard deviations on the means) of cadmium, copper and zinc in the foods analysed are presented in Table 6·3. The classification of food groups in Table 6·3 is the same as that used by Pickston *et al.* (1985). Ash weight concentrations of the three metals in foods are given in Appendix 6·1.

The mean of the coefficients of variation of the concentrations of cadmium, copper and zinc in food can be calculated from the data in Table 6·3, and can be taken to represent analytical scatter superimposed upon any remaining sample heterogeneity. They are 17% for cadmium, 12% for copper, and 8% for zinc. These coefficients of variation were thought to represent a satisfactory level of precision, given food's typically heterogeneous nature and the low absolute levels of cadmium in most foods.

Table 6·3

Mean wet weight concentrations of cadmium, copper and zinc (and their standard deviations) in individual food items. Ash weight concentrations of the three metals in each food are given in Appendix 6·1.

Food	Number of analyses	Cadmium (μg kg^{-1})		Copper (μg g^{-1})		Zinc (μg g^{-1})	
		Mean concn.	Standard deviation	Mean concn.	Standard deviation	Mean concn.	Standard deviation
Cereal-based products							
Bread (white)							
Brand # 1	2	8.34	0.92	1.03	0.02	6.03	0.25
Brand # 2	2	12.2	0.2	0.980	0.016	6.27	0.23
Bread (wholemeal)							
Brand # 1	2	17.7	0.9	1.98	0.18	12.6	1.6
Brand # 2	2	16.7	1.4	1.95	0.04	14.7	0.07
Cornflakes	3	6.68	0.48	0.548	0.027	1.61	0.05
Flour							
White	2	30.2	0.2	1.27	0.06	7.39	0.07
Wholemeal	2	38.9	0.5	3.45	0.18	24.4	0.2
Porridge (oats)	3	20.2	0.6	1.06	0.20	17.6	0.3
Rice (white, long grain)	3	6.02	0.88	0.536	0.116	13.2	0.3
Spaghetti, white	3	9.82	0.42	2.21	0.02	4.85	0.02
"Weet-bix"	3	59.1	1.6	4.11	0.53	32.7	1.9
Dairy products							
Butter	2	5.04	0.08	0.094	0.016	0.646	0.038
Milk	3	0.593	0.167	0.039	0.003	3.09	0.03
Drinks							
Cocoa[a]	9	179	40	31.3	1.6	69.1	5.0
Coffee (instant)	3	1.47	0.04	0.083	0.019	1.98	0.06
Tea	3	20.3	2.7	19.2	1.3	22.0	1.1
Fats and oils							
Margarine	2	3.10	2.79	0.037	0.001	0.093	0.038
Fruit							
Apples	3	0.861	0.275	0.267	0.011	0.170	0.002
Bananas	3	1.50	0.83	0.787	0.090	1.45	0.04
Oranges	3	0.72	0.03	0.385	0.067	0.469	0.114
Peaches (canned)	3	2.69	0.30	0.219	0.013	0.696	0.035
Pears	3	2.35	0.13	0.718	0.004	1.15	0.10

Table 6·3 continued...

Food	Number of analyses	Cadmium (μg kg^{-1})		Copper (μg g^{-1})		Zinc (μg g^{-1})	
		Mean concn.	Standard deviation	Mean concn.	Standard deviation	Mean concn.	Standard deviation
Meat, poultry, fish and eggs							
Beef							
Chuck steak	2	1.92	0.57	0.660	0.008	46.1	0.3
Liver	2	176	12	3.17	0.24	20.1	2.3
Porterhouse steak	2	1.66	0.14	0.501	0.034	36.5	1.5
Steak mince	2	2.09	0.12	0.537	0.029	37.2	1.3
Weiner schnitzel	2	2.24	0.59	0.752	0.042	26.6	1.1
Chicken (thighs)	3	1.56	0.03	0.478	0.082	9.50	0.26
Sheepmeat							
Lamb kidney	2	62.2	5.7	3.55	0.19	17.8	1.1
Lamb liver	2	70.1	11.0	45.1	5.3	25.0	2.3
Lamb shoulder	2	1.20	0.24	0.596	0.006	29.1	0.8
Mutton leg chops	2	1.72	1.03	0.802	0.010	31.0	0.8
Pork (rump steak)	3	2.19	0.14	0.777	0.091	16.3	0.4
Sausage meat (beef/mutton)	3	3.24	0.24	0.820	0.018	21.0	0.4
Orange roughy	3	4.17	1.95	0.228	0.107	3.67	0.12
Red cod	3	3.70	0.88	0.251	0.021	4.12	0.10
Sardines (canned)	3	10.4	0.9	0.974	0.032	12.9	1.2
Tuna (canned)	3	20.5	3.5	0.634	0.045	7.86	0.47
Eggs	3	1.65	0.71	0.535	0.019	9.88	0.38
Sweet foods and nuts							
Jam (raspberry)	3	7.97	0.88	0.387	0.034	1.21	0.08
Peanut butter	2	71.8	1.6	5.93	0.09	28.5	0.7
Sugar (white)	3	1.26	0.53	<0.02		0.731	0.242
Vegetables							
Cabbage	3	1.23	0.12	0.096	0.013	3.00	0.49
Carrots	3	14.4	8.5	0.367	0.147	1.77	0.70
Celery	3	0.372	0.064	0.278	0.047	0.733	0.027
Lettuce	3	10.4	0.5	0.414	0.019	2.56	0.06
Onions	3	96.1	11.6	0.631	0.039	2.04	0.04
Peas (frozen)	3	2.51	0.43	1.38	0.05	7.69	0.08
Potatoes	3	21.6	1.3	0.820	0.047	3.04	0.21
Tomatoes	3	9.04	1.08	0.393	0.033	1.12	0.03
Miscellaneous							
Vegemite	2	15.0	1.6	2.57	0.20	39.8	1.2
Water[b]	11	0.017	0.010	0.013	0.025	0.042	0.035

Notes: **a.** Two different brands analysed.
b. Mean of five tap and six kettle-water samples.

Concentrations of cadmium in all the foods analysed are well below the legal limit of 1 000 μg kg^{-1} (Table 6·3) (Anon. 1984). The highest ten concentrations are found in cocoa powder (179 μg kg^{-1}), beef liver (176 μg kg^{-1}), onions (96.1 μg kg^{-1}), peanut butter (71.8 μg kg^{-1}), lamb liver (70.1 μg kg^{-1}), lamb kidney (62.2 μg kg^{-1}), "weet-bix" (59.1 μg kg^{-1}), wholemeal flour (38.9 μg kg^{-1}), white flour (30.2 μg kg^{-1}) and potatoes (21.6 μg kg^{-1}). In terms of food groups the highest concentrations of cadmium are associated with cereal-based foods, beverages, root vegetables and offals (beef liver, lamb liver and lamb kidney); the lowest levels are found in fruits, muscle meats, dairy products, eggs and fats (Table 6·3).

Wholemeal flour and bread have more cadmium than white flour and bread; however, the wholemeal foods also contain more copper and zinc, metals which have the effect of reducing cadmium absorption through the gut if ingested concurrently (Spivey-Fox, 1988). Guthrie (1975) also noted that refined cereals contained reduced trace metal concentrations. This is due to the metal-rich outer layers (and germinal epithelia) of the grain being removed during the refining process.

Root vegetables (mean cadmium content 44.0 μg kg^{-1}) contain more cadmium than other vegetables (mean value 4.71 μg kg^{-1}). Cadmium can enter plants through the roots and the leaves. It has been previously found that in most plants, the highest accumulations of cadmium occur in the root tissues (Kabata-Pendias and Pendias, 1985).

Concentrations of cadmium in muscle meats are low—about 2 μg kg^{-1} (Table 6·3). Levels in beef liver, lamb liver and lamb kidneys are comparatively high (mean value 103 μg kg^{-1}), presumably because cadmium accumulates in these organs (sections 1·4·2 and 2·2·2b). Solly *et al.* (1981) also found that the highest concentrations of cadmium in sheep, cattle and pigs were located in the animals' kidneys and livers.

In terms of food groups, copper concentrations are highest in cereal-based foods, offals and some drinks; concentrations of zinc are highest in meat (muscle meat and offals), cereal-based foods and some drinks.

6·3·2 Daily dietary intakes of cadmium, copper and zinc

Estimates of the daily dietary intakes of cadmium, copper and zinc can be made by calculating mean concentrations of these metals in the main food groups, multiplying the means by the average weight of each food group ingested per day, and summing the products. The average daily food intake of 23–50 yr old males is about 2.5 kg, which in terms of energy is equivalent to 12.66 MJ (Pickston *et al.* 1985). Estimated daily intakes of the various food groups in New Zealand (assuming a total daily food intake of 2.5 kg) were calculated from the data of Pickston *et al.* (1985). These are listed in Table 6·4. Also given in Table 6·4 are the mean concentrations of cadmium, copper and zinc in the main food groups, the estimated contribution of these groups to the daily dietary intakes of cadmium, copper and zinc, and the overall estimated daily intakes of the three metals. In the case of drinks, it was assumed that 4 g of each beverage was mixed with 500 ml water.

Table 6·4

Estimated daily intakes of the various food groups assuming 2.5 kg of food is eaten[a], mean concentrations of cadmium, copper and zinc of these food groups, and calculated daily intakes of cadmium, copper and zinc.

Food group	Weight ingested per day (kg)[a]	Mean concentrations			Daily intakes		
		Cd ($\mu g\ kg^{-1}$)	Cu ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)	Cd (μg)	Cu (μg)	Zn (μg)
Cereal-based products	0.208	20.5	1.74	12.9	4.3	362	2 680
Dairy products	0.324	2.82	0.067	1.87	0.9	22	606
Drinks[b]	0.716	0.552	0.015	0.290	0.4	11	208
Fats and oils	0.029	3.10	0.037	0.093	0.1	1	3
Fruit	0.228	1.62	0.475	0.787	0.4	108	179
Meat, poultry fish and eggs	0.225	21.6	3.55	20.9	4.9	799	4 700
Sweet foods and nuts	0.138	27.0	2.11	10.2	3.7	291	1 410
Vegetables	0.377	19.5	0.547	2.74	7.4	206	1 030
Total intake					22.1	1 800	10 800

Notes: a. Data from Pickston *et al.* 1985.
b. Calculated assuming 4 g of each beverage (coffee, cocoa, tea) is mixed with 500 ml of water.

The estimated daily food-derived intake of cadmium assuming 2.5 kg of food is eaten is 22.1 μg. The World Health Organization's provisional tolerable intake of cadmium for a 60 kg person is 60–72 $\mu g\ day^{-1}$ (or 70–84 $\mu g\ day^{-1}$ for a 70 kg person) (FAO/WHO, 1972). The intake estimated in this study for Christchurch residents is 3–4 times below the WHO limit (Table 6·4).

Of ingested cadmium, about 6% is absorbed by the (adult) gut (section 1·4·2). Thus, the absorption of cadmium by Christchurch adults from food sources is likely to be in the region of 1.3 $\mu g\ day^{-1}$.

The food-derived cadmium intake estimated in this study is listed alongside other New Zealand estimates and recent overseas estimates in Table 6·5 (following page). It can be seen from the data in Table 6·5 that the dietary cadmium intake estimated in this study is very close in value to Guthrie and Robinson's (1977, 1978) value of 21 μg (based on a duplicate diet survey—section 2·2·2). Surprisingly, these two estimates are more or less identical to recently estimated dietary cadmium intakes of residents of the United Kingdom and the U.S.A. (both recalculated for 2.5 kg of food), implying that differences in food-derived cadmium intakes between countries may be small.

Table 6·5

Various estimates of the daily dietary intake of cadmium.

Location	Reference	Daily food consumption (kg)	Estimated daily cadmium intake (μg)
New Zealand			
	Guthrie & Robinson, 1977	(0.384 dry weight)	21
	Dick *et al.* 1978	2.50	12
	Pickston *et al.* 1985	1.66[a]	38
		2.50[b]	57
	This study, 1989	2.50	22
United Kingdom			
	Sherlock & Smart, 1986	1.44	12
		2.50[b]	21
U.S.A.			
	Spivey-Fox, 1988	2.35	20
		2.50[b]	21

Notes: **a.** Excluding oysters.
b. Recalculated for 2.5 kg of food.

The following problem becomes apparent when attempting to estimate cadmium intakes in cases when concentrations of cadmium in some of the food items analysed are found to be below the detection limit: if, for the purposes of the calculation, cadmium concentrations in these foods are assumed to be zero, a low intake estimate will result; if, on the other hand, the detection limit concentrations are used, the result will be a high estimate. The method of FAAS, used to determine concentrations of cadmium in the three previous New Zealand studies listed in Table 6·5, is insufficiently sensitive to accurately measure the levels of cadmium in most food items. Dick *et al.* (1977) reported that cadmium was detected in only 18 of a total of 116 composite food samples. Thus, the (apparently) low cadmium intake estimate of Dick *et al.* (1977) could be due to the authors assigning a cadmium concentration of zero to food composites in which cadmium was not detected (the method of the intake estimate was not fully described). Pickston *et al.* (1985) assumed that concentrations of cadmium were zero in foods in which the metal was not detected (which would tend to produce a low estimate); their (apparently) high cadmium intake estimate could be a result of insufficient analytical sensitivity to the low concentrations of cadmium in most foods. In this survey, the analytical method used was GFAAS, and cadmium was detected in all food samples.

The main error in the daily cadmium intake estimate calculated in this study is probably the assumption (implicit in the calculations of mean cadmium concentrations) that the same quantity of each item in a given food group is eaten. This error would be greatest

when a rarely consumed item in a particular food group contains a markedly higher (or lower) cadmium concentration than the remaining items in the group. This could be the case in the calculation of the mean cadmium level in the "meat, poultry, fish and eggs" food group. In this group, beef liver, lamb liver and lamb kidneys contain substantially more cadmium than the other foods. Implicit in the daily intake calculation is the assumption that offals comprise 18% of the "average" New Zealand intake of the "meat, poultry, fish and eggs" group (*i.e.* 3 of the 17 foods are offals). The true figure for New Zealand could be somewhat lower than this. Unfortunately, no data has been collected which describes the "typical New Zealand diet" in enough detail for it to be possible to make direct estimates of the contributions of each of the food items studied to the dietary cadmium intake (MacNeill, 1989). However, it can be calculated from the data of Sherlock and Smart (1986) that offals represent 17% of meat, poultry, fish and egg consumption in the "average United Kingdom diet".

As cadmium concentrations in oysters were not measured, the daily intake of cadmium estimated in this study should be taken to apply to non-oyster eaters. Consumption of oysters is seasonal and varies from person to person (section 2·2·2c). Additionally, cadmium concentrations in oysters are highly variable, depending both on species and location. Assuming that oysters contain on average about 1 $\mu gCd\ g^{-1}$ (section 2·2·2c), ingestion of two 10 g oysters each day would be sufficient to double an individual's cadmium intake.

Cigarettes (though not strictly a food item) also have the potential to boost daily cadmium intakes. One packet of cigarettes was analysed (by the same method as food samples) and was found to contain 1.04 $\mu gCd\ g^{-1}$. Brooks and Trow (1979) analysed 49 New Zealand brands of cigarettes and reported mean cadmium levels ranging from 0.23 to 0.56 $\mu g\ g^{-1}$ (section 2·2·2d). It is difficult to estimate cigarette-derived cadmium intakes directly from the cadmium concentrations in cigarettes. Volatilization of cadmium (or conversion to particulates) during smoking may be incomplete, not all of the smoke will be inhaled, and much of the inhaled smoke is exhaled again (Brooks and Trow, 1979). Nevertheless, the smoking of 20 (1 $\mu gCd\ g^{-1}$) cigarettes each day has been estimated to result in an inhalation of 3 $\mu gCd\ day^{-1}$ (Schulte-Schrepping and Piscator, 1985). The lungs absorb 25–50% of inhaled cadmium (section 1·4·2). Thus, bodily absorption of cadmium by a person who smoked 20 cigarettes per day (0.75–1.5 $\mu gCd\ day^{-1}$) could equal or exceed that person's absorption of cadmium from food sources (1.3 $\mu gCd\ day^{-1}$).

Copper and zinc can be thought of in terms of recommended daily intakes rather than of toxicities, as both metals are metabolically useful. The Nutrition Advisory Committee have estimated that adults require 8–10 $mgZn\ day^{-1}$ for bodily equilibrium (North *et al.* 1983). The intake estimated in this study was 10.8 $mgZn\ day^{-1}$ (Table 6·4). Other estimates

of New Zealand dietary zinc intakes have been made by Guthrie and Robinson (1977), Dick *et al.* (1978) and Pickston *et al.* (1985); and are 10 mg day^{-1}, 14.8 mg day^{-1} and 16.3 mg day^{-1}, respectively (adjusted for 2.5 kg of food). It is likely, then, that New Zealanders consuming a balanced diet will be amply supplied with zinc.

The minimum daily copper requirement has been estimated by the Nutrition Advisory Committee to be 30 μg kg^{-1} day^{-1} in adults (North *et al.* 1983). The copper intake estimated in this study was 1 800 μg day^{-1} for 2.5 kg of food (Table 6·4). A 70 kg adult (70 kg being a typical weight for a person who consumes 2.5 kg of food daily) would require minimum of 2 100 μgCu day^{-1}. The estimated copper intake can be adjusted for possible losses during processing and analysis of food samples. If it is assumed that an average of 87% of the copper in all food samples was recovered, as was the case for certified reference hay (Table 6·2), the estimated daily copper intake could be adjusted up to 2 070 μg. This figure is still slightly below the minimum daily requirements of a 70 kg person. Slight copper deficiencies in New Zealand foods (compared with overseas foods) have previously been noted by Guthrie (1975) and Guthrie and Robinson (1978). Other estimates of New Zealanders' dietary copper intakes are 1 500 μg day^{-1} (Guthrie and Robinson, 1977), 2 460 μg day^{-1} (Dick *et al.* 1978), and 2 320 μg day^{-1} (Pickston *et al.* 1985) (adjusted for 2.5 kg of food). The mean value of all four estimates is 2 090 μgCu day^{-1}, which can be compared with the minimum requirement of 2 100 μgCu day^{-1}. It is apparent that the average New Zealander's daily copper intake is likely to be "just sufficient" for metabolic needs.

6·3·3 Contributions of each food group to daily intakes

The percentage contributions of each food group to the daily intakes of cadmium, copper and zinc were calculated from the data in Table 6·4 and are given in Appendix 6·2. Figure 6·1 is derived from the data in Appendix 6·2.

Figure 6·1

Contribution of each food group to the total daily dietary intakes of cadmium, copper and zinc.

It can be seen from the data in Appendix 6·2 and from Figure 6·1 that 93% of the daily cadmium intake is supplied by four food groups: vegetables (34%); meat, poultry, fish and eggs (22%); cereal-based foods (20%); and sweet foods and nuts (17%).

Potatoes, which comprise 7.1% of the New Zealand diet (Pickston *et al.* 1985) would contribute about 50% of the cadmium derived from vegetables. Beef liver, lamb liver and lamb kidneys are responsible for 82% of the cadmium intake figure of the group "meat, poultry, fish and eggs". Excluding offals, the daily cadmium intake estimate would fall to 18.1 μg (from 22.1 μg). Similarly, peanut butter accounts for 84% of the cadmium intake figure of the group "sweet foods and nuts".

Relative contributions of each food group to daily copper intakes are very similar to contributions of each food group to zinc intakes (Appendix 6·2 and Figure 6·1). "Meat, poultry, fish and eggs" contribute 44% of the total daily intake of both metals. However, beef liver, lamb liver and lamb kidneys are responsible for most (82%) of the copper intake derived from "meat, poultry, fish and eggs" (whereas offals account for only 18% of the zinc intake figure in this food group). Without offals, daily copper intakes would fall to 1 140 μg. It can also be calculated that vegetarians who substituted dietary intakes of meat, poultry, fish and eggs with items of the other seven food groups (in equal amounts) would ingest about the same amount of cadmium (19.5 μg day^{-1}) but substantially less copper (1 100 μg day^{-1}) and zinc (7 120 μg day^{-1}) than persons consuming the "normal" diet.

Other than from "meat, poultry, fish and eggs", copper and zinc are mainly derived from cereal-based foods (about 22% of the daily intakes of the two metals), sweet foods and nuts (about 15%) and vegetables (about 10%) (Appendix 6·2 and Figure 6·1). Peanut butter accounts for 91% of the copper and zinc intake estimates in the group "sweet foods and nuts".

Of the four food groups which contribute the most cadmium to the daily dietary intake, copper and zinc are relatively abundant in "meat, poultry, fish and eggs", "cereal-based foods" and "sweet foods and nuts", and would have the effect of decreasing absorption of cadmium from these foods (Table 6·3) (Spivey-Fox, 1988). However, copper and zinc are relatively deficient in vegetables, the food group which makes the greatest contribution (34%) to the dietary cadmium intake (Table 6·3 and Figure 6·1). In addition to this, vegetables are one of the three food groups most likely to accumulate cadmium from phosphatic-fertilizers applied to farmland (the other two food groups are cereals and offals) (Sherlock and Smart, 1986; section 2·1·2e).

6.4 Conclusion

Concentrations of cadmium, copper and zinc were measured in a range of food items purchased in Christchurch. The highest concentrations of cadmium were found in offals, root vegetables, some cereal-based foods, cocoa powder and peanut butter. The lowest concentrations of cadmium were found in fruits, muscle-meats, dairy products and fats.

Dietary intakes of the three metals, based on a total daily food consumption of 2.5 kg, were estimated to be 22.1 μgCd day^{-1}, 1 800 μgCu day^{-1} and 10 800 μgZn day^{-1}.

The cadmium dietary intake figure is almost identical to recent overseas (U.K. and U.S.A.) estimates, and to an earlier New Zealand estimate made by Guthrie and Robinson (1977). Most (93%) of the daily cadmium intake is derived from vegetables (34%), cereal-based foods (20%), "meat, poultry, fish and eggs" (22%) and "sweet foods and nuts" (17%). Of these groups, only vegetables are comparatively deficient in copper and zinc—metals which inhibit the absorption of cadmium through the gut. Potatoes, offals and peanut butter contribute significant amounts of cadmium to the cadmium intake figures of the food groups "vegetables", "meat, poultry, fish and eggs" and "sweet foods and nuts" (respectively).

Consumption of a few oysters daily could easily double an individual's intake of cadmium, and the smoking of 20 cigarettes per day could double the amount of cadmium absorbed by the smoker.

The estimated intake of zinc (10 800 $\mu g\ day^{-1}$) is slightly above the amount required by adults (8–10 $mg\ day^{-1}$), whereas the estimated intake of copper (1 800–2 070 $\mu g\ day^{-1}$) is slightly below the minimum requirement of a 70 kg adult (2 100 $\mu g\ day^{-1}$). It has previously been found that New Zealand foods generally contain less copper than overseas foods.

Most of the daily intakes of copper and zinc are derived from the food groups "meat, poultry, fish and eggs", "cereal-based foods", "vegetables" and "sweet foods and nuts". Due to the high contribution of the "meat, poultry, fish and eggs" food group to dietary copper and zinc intakes in New Zealand (44%), and to the low copper content of New Zealand foods generally, persons consuming diets low in meat or vegetarian diets would probably become deficient in copper and zinc.

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6·6 Appendices

Appendix 6·1 (section 6·3·1)

Mean ash weight concentrations of cadmium, copper and zinc (and their standard deviations) in individual food items.

Food	Number of analyses	Cadmium ($\mu g\ g^{-1}$)		Copper ($\mu g\ g^{-1}$)		Zinc ($\mu g\ g^{-1}$)	
		Mean concn.	Standard deviation	Mean concn.	Standard deviation	Mean concn.	Standard deviation
Cereal-based products							
Bread (white)							
Brand # 1	2	0.486	0.050	59.6	1.6	351	13
Brand # 2	2	0.620	0.012	50.1	0.9	321	12
Bread (wholemeal)							
Brand # 1	2	0.865	0.105	96.5	2.0	612	36
Brand # 2	2	0.739	0.060	85.8	1.1	645	4
Cornflakes	3	0.275	0.022	22.6	1.1	66.4	1.2
Flour							
White	2	5.33	0.04	224	11	1 310	14
Wholemeal	2	2.60	0.02	231	13	1 630	21
Porridge (oats)	3	1.15	0.04	60.3	13	1 000	9

Appendix 6·1 continued...

Food	Number of analyses	Cadmium (μg g^{-1})		Copper (μg g^{-1})		Zinc (μg g^{-1})	
		Mean concn.	Standard deviation	Mean concn.	Standard deviation	Mean concn.	Standard deviation
Rice (white, long grain)	3	1.03	0.18	93.0	27.6	2 270	218
Spaghetti, white	3	1.73	0.08	388	4	854	4
"Weet-bix"	3	2.41	0.07	167	21	1 340	76
Dairy products							
Butter	2	0.360	0.009	6.53	1.04	44.8	2.6
Milk	3	0.081	0.024	5.41	0.42	422	2
Drinks							
Cocoa[a]	9	2.00	0.47	350	12	776	79
Coffee (instant)	3	0.012	0.001	0.682	0.232	16.1	1.7
Tea	3	0.362	0.049	342	24	392	21
Fats and oils							
Margarine	2	0.369	0.413	4.12	0.81	9.85	1.77
Fruit							
Apples	3	0.387	0.119	120	6	76.2	1.8
Bananas	3	0.095	0.051	49.8	0.5	92.5	11.8
Oranges	3	0.174	0.036	90.8	6.3	109	5
Peaches (canned)	3	0.286	0.049	23.3	1.2	73.8	4.1
Pears	3	0.813	0.037	248	6	398	33
Meat, poultry, fish and eggs							
Beef							
Chuck steak	2	0.197	0.057	67.9	1.4	4 750	10
Liver	2	15.5	0.1	280	1	1 770	80
Porterhouse steak	2	0.170	0.012	51.1	4.2	3 710	100
Steak mince	2	0.240	0.011	61.7	2.4	4 280	90
Weiner schnitzel	2	0.206	0.052	69.1	4.7	2 450	130
Chicken (thighs)	3	0.210	0.002	64.7	10.7	1 290	40
Sheepmeat							
Lamb kidney	2	5.33	0.33	305	25	1 530	50
Lamb liver	2	5.58	0.97	3 590	490	1 990	212
Lamb shoulder	2	0.142	0.030	71.1	1.8	3 440	110
Mutton leg chops	2	0.164	0.098	76.4	1.1	2 950	80
Pork (rump steak)	3	0.217	0.014	77.0	9.1	1 620	40
Sausage meat (beef/mutton)	3	0.094	0.006	23.8	0.6	610	11

Appendix 6·1 continued...

Food	Number of analyses	Cadmium (μg g^{-1})		Copper (μg g^{-1})		Zinc (μg g^{-1})	
		Mean concn.	Standard deviation	Mean concn.	Standard deviation	Mean concn.	Standard deviation
Orange roughy	3	0.443	0.205	24.0	11.8	391	15
Red cod	3	0.340	0.085	23.0	1.4	377	3
Sardines (canned)	3	0.497	0.024	46.2	0.8	610	34
Tuna (canned)	3	1.65	0.28	51.0	3.8	633	46
Eggs	3	0.179	0.078	58.1	1.9	1 070	37
Sweet foods and nuts							
Jam (raspberry)	3	3.74	0.40	182	16	571	38
Peanut butter	2	2.29	0.04	189	1	910	28
Sugar (white)[b]	3	20.0	11.1	<312		12 700	10 400
Vegetables							
Cabbage	3	0.226	0.013	17.6	2.3	548	56
Carrots	3	1.44	1.17	35.4	20.2	171	100
Celery	3	0.038	0.006	28.6	4.1	75.4	1.9
Lettuce	3	1.98	0.13	78.6	4.5	487	54
Onions	3	19.5	1.8	129	9	415	9
Peas (frozen)	3	0.384	0.066	211	4.5	1 170	35
Potatoes	3	2.12	0.16	80.4	7.7	298	33
Tomatoes	3	1.22	0.06	53.9	10.1	153	18
Miscellaneous							
Vegemite	2	0.139	0.052	23.4	4.5	363	86

Notes: **a.** Two different brands analysed.
b. Very low ash weight.

Appendix 6·2 (section 6·3·2)

Percentage contribution of each food group to the daily intake of cadmium, copper and zinc.

Food group	Percentage of total intake		
	Cadmium	Copper	Zinc
Cereal-based products	19.5	20.1	24.8
Dairy products	4.1	1.2	5.6
Drinks	1.8	0.6	1.9
Fats and oils	0.5	0.1	0
Fruit	1.8	6.0	1.7
Meat, poultry, fish and eggs	22.2	44.4	43.5
Sweet foods and nuts	16.7	16.2	13.1
Vegetables	33.5	11.4	9.5
Total	100.1[a]	100	100.1[a]

Note: **a.** Rounding error.

CHAPTER 7
SEASONAL VARIATIONS IN THE CONCENTRATIONS OF CADMIUM, COPPER, LEAD AND ZINC IN CHRISTCHURCH AIR

7·1 Introduction

Metals and their compounds exist in the atmosphere in three different physical forms: vapours, liquid droplets (mists) and solid particulate matter. Of these, the majority of metallic air pollution is associated with solid particulates (Harrison, 1986a). Airborne cadmium is predominantly associated with particles of 0.6–10 μm diameter, and of this size range is most concentrated in particles of about 2 μm diameter (Davidson, 1980; Nriagu, 1980). Because human lungs trap particles in the diameter range 0.4–4.7 μm, it follows that most atmospheric cadmium exists in the respirable form (Noller and Bloom, 1980; Nriagu, 1980). Between 25 and 50% of inhaled cadmium is absorbed by the lungs (section 1·4·2).

Natural and anthropogenic sources of cadmium to the atmosphere are discussed in section 1·3·1. One of the most important anthropogenic sources is combustion (Nriagu and Pacyna, 1988; section 1·3·1). In terms of combustion as a source of cadmium to the atmosphere of Christchurch city, the following points are worthy of note:

1. Serious air pollution often occurs over Christchurch city in the winter months (May to August). During about 60% of winter nights, interactions between prevailing climatic conditions and Christchurch's topology are such that a stagnant pool of cold air forms over the city, which has the effect of inhibiting the dispersal of (mainly combustion-derived) pollutants. This phenomenon is known as a "temperature-inversion" because, when it occurs, the heat profile of the atmosphere decreases with height (Alcorn *et al.* 1966; Pullen, 1977; Ryan, 1977).
2. Because household fires are extensively used on winter nights, Christchurch air pollution during winter temperature-inversions is characterized by the presence of various products of coal and wood combustion, the most serious of which in terms of human health are considered to be smoke and sulphur dioxide (Anon. 1986).
3. Petrol combustion in car engines is also a significant source of pollutants to Christchurch air (primarily nitric oxide, nitrogen dioxide, carbon monoxide, unburnt hydrocarbons and lead) (Anon. 1986; Day, 1977; Fergusson *et al.* 1980). Once again, due to the effects of temperature-inversions, the highest concentrations of these pollutants occur during the winter months.

This study was designed to monitor seasonal variations in, and identify some of the factors which influence, concentrations of cadmium in Christchurch air. Concentrations of copper, lead and zinc in Christchurch air were also measured, due to cadmium's geochemical association with these metals (section 1·2·1).

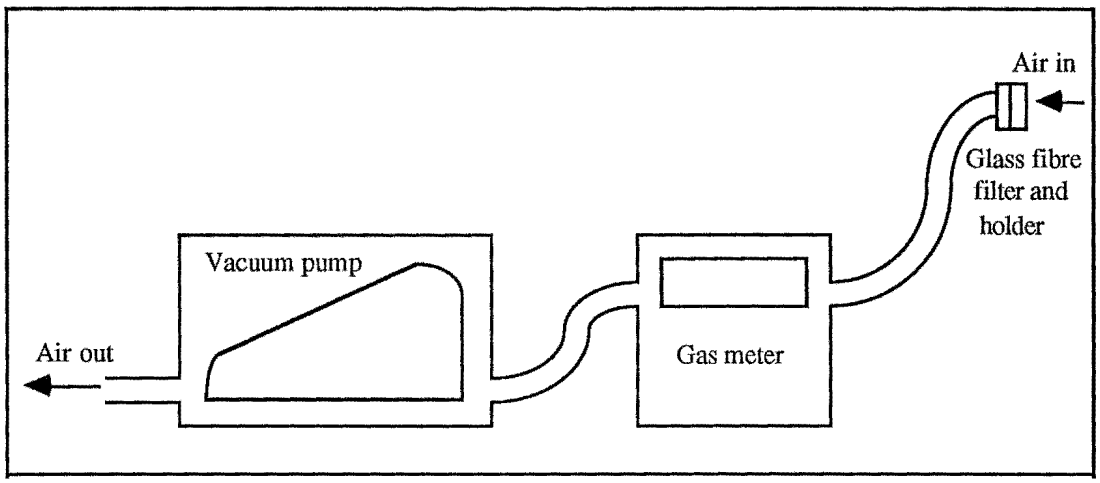
7.2 Method

7.2.1 Sample collection

Airborne particulates were collected by the *high-volume* sampling technique onto 50 mm diameter AGF Gelman glass-fibre filters. A schematic diagram of the sampling apparatus is given in Figure 7·1.

Figure 7·1

Schematic diagram of the apparatus used for the collection of airborne particulates.



Glass-fibre filters have been estimated to collect 99.9% of particles of 0.03 μm diameter travelling at a face velocity of 5 cm s^{-1} (Harrison, 1986b). Filters were held in a stainless-steel holder (Figure 7·1). During rain, a plastic cover was fitted over the holder to prevent rain from striking the filter; care was taken to ensure that the rain-cover did not obstruct air-flow to the filter. The pump was powered by electricity. Air leaving the pump was vented a considerable distance from the air intake and in the opposite direction. The gas meter (Figure 7·1) was calibrated prior to use. During sampling, the sample holder and filter were positioned 2 m above ground level. Each sample was collected for 24 hr, after which time approximately 115 m^3 of air had been drawn through the filter by the vacuum pump.

Before use, filters were brought to constant humidity over dried silica-gel and weighed (to five decimal places) in a class 100 Clean Room. After sample collection, the procedure was repeated. Before and after sample collection, filters were stored in clean plastic bags. Disposable plastic gloves were used at all times when handling filters. Filters destined for later use as analytical blanks were loaded into and unloaded from, the sample holder without a sample having been taken.

Two Christchurch sites were chosen for sample collection, and these are shown in Appendix 3·1 (inside back cover). Samples were collected at the first site, in the suburb of Avonside, for a total of 60 days during June 1987–May 1988; and samples were collected at the second site, in the suburb of Huntsbury, for a total of 40 days during June 1988–January 1989. At both locations, five samples were collected on five consecutive days near

the end of each month. The collection time spanned from 5 pm one day to 5 pm the next. The suburb of Avonside is located on the plain, and is less than 15 m above sea level in height. In contrast, the suburb of Huntsbury is situated on a hillside—the sampling site itself was about 100 m above sea level. This height is usually regarded as being above the thermal inversion layer (when it occurs). Throughout this Chapter, the sampling site in the suburb of Avonside will be referred to as site 1, and that in the suburb of Huntsbury will be referred to as site 2.

Climatological data (rainfall, air temperature, mean wind speed and wind direction) for Christchurch on the dates and times that samples were collected was purchased from the New Zealand Meteorological Service.

7·2·2 Digestion and analysis of samples

Each sample (a filter with collected particulate matter) was boiled for 30 min in 15 ml of 4 M AR nitric acid. The solution was then filtered (through a nitric acid and double-distilled water washed Whatman 540 filter paper) and washed with double-distilled water to a total volume of 25 ml.

Zinc concentrations in the extracts were determined by FAAS, using the parameters given in Chapter 14. Cadmium, copper and lead concentrations were determined by GFAAS, using the parameters given in section 3·2·2 and Chapter 14. Background correction was used in all cases. Standards were prepared from 1 000 $\mu g\ ml^{-1}$ stock solutions, and made up to the same acid strength as the samples. Unused glass-fibre filters were digested for use as sample blanks. Glass-fibre filters have previously been found to contain analytically significant levels of zinc and lead (Harrison, 1986a). However, these metals were not detected by the methods outlined in blank solutions made from unused glass-fibre filters in this study.

Several (Whatman No. 541 4.25 cm) cellulose filters were spiked with varying concentrations of cadmium, copper, lead and zinc. Filters were first acid-washed (4 M AR nitric acid), rinsed thoroughly with double-distilled water, and dried. Standard solutions, each containing different concentrations of cadmium, copper, lead and zinc in double-distilled water, were prepared from stock solutions. A measured volume of the appropriate solution was added to each filter, which was then dried. It was found that glass-fibre filters could not be spiked by this method, as they proved to be extremely water-repellent. The spiked cellulose filters and two certified-reference air filters (AIR 3/1, International Atomic Energy Agency, Vienna) were digested and analysed for the purpose of assessing analytical precision and bias. The results of these analyses are given in Table 7·1. The degree of analytical scatter (represented by the coefficients of variation) in the determinations of the concentrations of cadmium, copper, lead and zinc was found to be fairly low (Table 7·1). The recoveries of cadmium, copper, lead and zinc indicated that the analytically determined concentrations of these metals were unlikely to differ significantly from their true concentrations.

Table 7·1

Comparison of assumed concentrations of cadmium, copper, lead and zinc in spiked cellulose filter papers and in certified-reference air filter AIR 3/1 with concentrations determined in this study.

Material	Cadmium	Copper	Lead	Zinc
Certified-reference material AIR 3/1				
"True" concn. (μg filter^{-1})	10	46[a]	105	143
Determined concns. (μg filter^{-1})				
Filter 1	11.3	45	120	141
Filter 2	10.5	47	123	141
Coefficient of variation[b] (%)	5	3	2	0
Mean recovery (%)	109	100	116	99
Spiked cellulose filters				
Spiked concns. (μg filter^{-1})				
Filters 1 & 2	0.001	0.075	0.105	0.450
Filters 3 & 4	0.005	1.00	5.00	5.00
Filters 5 & 6	0.100	2.00	10.0	10.0
Filters 7 & 8	0.750	12.5	25.0	25.0
Filters 9 & 10	1.50	25.0	50.0	50.0
Determined concns. (μg filter^{-1})				
Filter 1	<0.003	0.070	<0.1	0.542
Filter 2	<0.003	0.088	<0.1	0.500
Filter 3[c]				
Filter 4	0.006	0.990	5.00	4.02
Filter 5	0.106	2.05	10.2	13.4
Filter 6	0.112	1.84	9.84	9.22
Filter 7	0.756	10.9	25.8	23.8
Filter 8	0.710	10.0	21.0	23.0
Filter 9	1.34	20.0	42.6	46.0
Filter 10	1.45	20.7	40.6	45.6
Mean recovery (%)	103	93	93	101
Mean coefficient of variation (%)[d]	5	8	7	9

Notes: **a.** Non-certified value.
b. 100 x standard deviation/mean.
c. Sample destroyed during digestion.
d. Mean of the coefficients of variation for each pair of filters.

7·3 Results and discussion

7·3·1 Summary statistics

Two different concentration measurements were made in relation to each metal: the concentration of a given metal in the air (expressed in units of ng m^{-3}), and the concentration of that metal per gram of collected particulate matter (expressed in $\mu g\ g^{-1}$). The complete data sets describing the concentrations (ng m^{-3} *and* $\mu g\ g^{-1}$) of cadmium, copper, lead and zinc, the total weight of material collected in 24 hr, and the climatological parameters rainfall, air temperature, mean wind speed and mean wind direction for each of 60 days at site 1 and 40 days at site 2 are given in Appendices 7·1 and 7·2. The variables "rainfall", "mean wind speed" and "mean wind direction" apply to the actual times that samples were being taken (*i.e.* 5pm–5pm), whereas "air temperature" is the temperature at 5 pm on the first of the two sampling days. Statistics summarizing the data sets in Appendices 7·1 and 7·2 are presented in Tables 7·2 and 7·3.

Table 7·2

Summary statistics describing the concentrations (ng m^{-3} and $\mu g\ g^{-1}$) of cadmium, copper, lead and zinc, the weight of matter collected in 24 hr, and various meteorological parameters relating to the survey of airborne particulates at sampling site 1 (n=60).

Variable	Arithmetic mean	Standard deviation	95% error on mean	Geometric mean	Range Lowest	Range Highest
Concentration in air (ng m^{-3})						
Cadmium	0.844	1.18	±0.305	0.516	0.110	6.29
Copper	16.2	13.8	±3.6	12.5	2.64	87.7
Lead	233	251	±65	155	28.9	1 280
Zinc	74.0	121	±31.3	47.4	10.0	903
Concentration in particulates ($\mu g\ g^{-1}$)						
Cadmium	31.8	37.5	±9.7	21.6	2.56	235
Copper	625	514	±133	490	100	3 260
Lead	7 130	3 400	±877	6 320	1 440	15 300
Zinc	2 760	3 500	±900	1 950	532	21 900
Weight collected in 24 hr	3.70	2.86	±0.74	2.87	0.49	14.0
Rainfall (mm) (5pm–5pm)	1.6	4.7	±1.2		0	30.9
Air temperature at 5pm (°C)	13	5	±1	12	3	24
Mean wind speed (5pm–5pm) (kts)	8	4	±1	7	1	19

Table 7·3

Summary statistics describing the concentrations (ng m^{-3} and $\mu g\ g^{-1}$) of cadmium, copper, lead and zinc, the weight of matter collected in 24 hr, and various meteorological parameters relating to the survey of airborne particulates at sampling site 2 (n = 40[a]).

Variable	Arithmetic mean	Standard deviation	95% error on mean	Geometric mean	Range Lowest	Range Highest
Concentration in air (ng m^{-3})						
Cadmium	0.468	0.464	±0.148	0.305	0.043	1.89
Copper	25.0	46.7	±15.8	8.22	0.449	188
Lead	77.6	35.9	±11.5	70.2	18.7	184
Zinc	25.9	15.4	±4.9	22.4	8.11	77.0
Concentration in particulates ($\mu g\ g^{-1}$)						
Cadmium	34.0	36.0	±11.5	20.4	1.45	193
Copper	1 430	2 450	±830	520	30.6	10 400
Lead	5 540	3 300	±1 060	4 820	1 180	18 700
Zinc	1 830	1 360	±430	1 500	530	6 470
Weight collected in 24 hr	2.07	1.24	±0.40	1.75	0.34	6.20
Rainfall (mm) (5pm–5pm)	0.6	1.3	±0.4		0	4.7
Air temperature at 5pm (°C)	15	6	±2	13	5	29
Mean wind speed (5pm–5pm) (kts)	9	4	±1	8	2	17

Notes: a. N = 36 for copper, as some outliers were removed.

In the case of copper concentrations (ng m^{-3} and $\mu g\ g^{-1}$) at site 2, a total of eight high observations (copper data for 20–21 and 23–24 June, 24–25 July and 23–24 September 1988) were removed from the data sets prior to the calculations of summary statistics. These were identified as outliers (at a 95% confidence level) by the method of Grubbs (1969). This procedure is outlined in Appendix 7·3. Although the excessively high copper concentrations represented by the outliers could have been caused by real variations in the amounts of copper in the air at site 2, it was thought more likely that intermittent copper contamination during sample digestion and/or analysis had occurred, as the samples for the months June–September 1988 were analysed in one batch. The samples in question appear to have remained uncontaminated by cadmium, lead or zinc.

The following observations can be made from the data in Tables 7·2 and 7·3 and that in Appendices 7·1 and 7·2:

1. The geometric mean concentrations of cadmium are 0.516 ng m^{-3} in air from site 1 and 0.305 ng m^{-3} in air from site 2 (range 0.043–6.29 ng m^{-3}). As was the case for the house-dust data (section 4·3·1), geometric means are likely to represent "true" means

more accurately than arithmetic means because most of the data sets are positively skewed (the two exceptions are the data sets of the variables "air temperature" and "mean wind speed"). Concentrations of cadmium in rural air are reported to be generally less than 1.0 ng m^{-3}, whereas concentrations in the air of urban areas usually fall within the range 1–50 ng m^{-3}, depending on the degree of industrialization (Nriagu, 1980). The arithmetic mean concentration of cadmium in urban air of the U.S.A. has been given by Harrison (1986) as 2 ng m^{-3}. The arithmetic mean ambient cadmium concentration found in this survey is about 0.66 ng m^{-3} (average of both sites' means). This figure is lower than the mean concentrations found in most urban areas of the world, but similar to values quoted for the world's rural areas (as listed by Nriagu, 1980). For example, cadmium concentrations in the air of Chedron (Nebraska), Sutton (England) and rural areas of Sweden have been reported to be 0.6, 0.4 and 0.9 ng m^{-3}, respectively. It is probable that the low concentrations of cadmium in Christchurch air are related to Christchurch's (comparatively) low degree of industrialization.

2. The yearly respiratory intake of adult humans has been estimated to be about 8 050 m^3 (mean of the estimates for men and women) (Snyder *et al.* 1975). From this figure and from the average of the geometric mean cadmium concentrations at sites 1 and 2 (0.41 ng m^{-3}), it can be calculated that adults in Christchurch are likely to inhale about 3.3 μgCd $year^{-1}$ (assuming that the data for sites 1 and 2 can be taken to be true for the rest of Christchurch). Of this, between 25 and 50% will be absorbed: 0.83–1.65 μg $year^{-1}$ (section 1·4·2). Dietary absorption of cadmium by Christchurch adults was estimated in section 6·3·2 to be 1.3 μg day^{-1}, which is equivalent to 475 μg $year^{-1}$. The estimated absorption of cadmium from airborne particulates is only 0.17–0.35% of this figure. Hence, absorption of cadmium by Christchurch residents from airborne particulates is likely to be negligible when compared with absorption of the metal from food sources.
3. The geometric mean concentrations of cadmium in airborne particulate matter are 21.6 μg g^{-1} (site 1) and 20.4 μg g^{-1} (site 2). Concentrations of cadmium in airborne particulate matter are higher than levels in soil or dust (section 3·3·1) because the finest particles (those most likely to become airborne) contain the highest concentrations of cadmium (section 3·3·3c). Particulate concentrations of cadmium have been reported to vary depending both on the source of the cadmium and the location. The highest airborne particulate cadmium concentrations (μg g^{-1}) are found not in urban air, but in the air at remote locations, reflecting the fact that in remote areas a greater relative proportion of airborne matter is represented by the smallest size fractions (Nriagu, 1980). Anthropogenic dispersal processes cause a greater proportion of coarse particles to be liberated to the atmosphere in urban areas than is usually the case for remote areas. Arithmetic mean particulate cadmium concentrations found in this survey (31.8 and 34.0 μg g^{-1}) are slightly higher than the (arithmetic) mean concentration for urban areas of the U.S.A., given by Nriagu

(1980) as 24 $\mu g\ g^{-1}$. A possible reason for this is that there may be a smaller number of (anthropogenic) particle-dispersal processes occurring in Christchurch than in most urban areas of the U.S.A.

Comparison can be made between the site 2 data (collected during June 1988–January 1989) and the site 1 data for the same months of the preceding year. Summary statistics describing the site 1 data for the months June 1987–January 1988 are given in Appendix 7·4. Direct comparison of the site 2 data (Table 7·3) with the site 1 data for June 1987–January 1988 (Appendix 7·4) reveal that there are statistically significant differences between the two data sets (at a 95% confidence level) in the ambient concentrations ($ng\ m^{-3}$) of lead and zinc (both are higher at site 1 than at site 2). The probabilities of the means belonging to different populations were calculated by computer (using a two-tailed two-group paired t-test) to be 99.6% for lead and 99.0% for zinc. An obvious hindrance to the interpretation of this direct comparison is that meteorological patterns differ from year to year; however, values of the variables "rainfall", "mean wind speed" and "air temperature" do not differ significantly between the two data sets. Given this fact, possible explanations for the higher ambient lead and zinc concentrations at site 1 than at site 2 are as follows:

1. The proportion of houses with galvanized-iron roofs is about the same in Avonside (site 1) as it is in Huntsbury (site 2), and the three nearest houses to both sampling sites had galvanized-iron roofs. However, the galvanized-iron roof of the house nearest to sampling site 1 was unpainted. The higher concentrations ($ng\ m^{-3}$) of zinc in the air at site 1 could be caused by aeolian erosion of the surface of this roof (sections 4·3·1 and 4·3·3c and Chapter 13).
2. Sites 1 and 2 were an equal distance (both about 30 m) from the nearest road, and the traffic density at both sites appeared to be similar. However, site 2 was located on a bank about 5 m above the road, and a tall hedge separated it from the road. In contrast, site 1 was in clear view of the road and on the same level as it. These facts suggest that lead derived from petrol constituted a greater fraction of the airborne lead at site 1 (sections 4·3·2 and 4·3·3d).

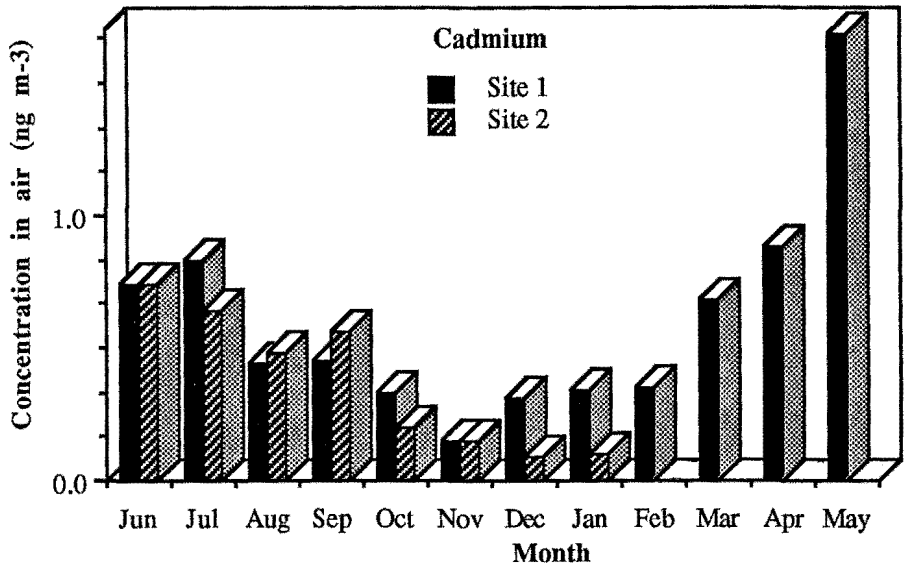
The mean weight of material collected each 24 hr period at site 1 during June 1987 to January 1988 is different from that collected at site 2 (June 1988 to January 1989) at a 94% confidence level. More material was collected per 24 hr period at site 1. This is likely to be because site 1 is always beneath the winter-time thermal inversion layer (when it occurs) whereas site 2 is usually above it (section 7·1).

7·3·2 Monthly variations

A list of monthly means, standard deviations, confidence intervals and medians of the metal concentrations ($ng\ m^{-3}$ and $\mu g\ g^{-1}$) and the variables "rainfall", "air temperature" and "mean wind speed" is presented in Appendix 7·5. Figures 7·2 and 7·3 are derived from the monthly median values listed in this data. (Median, rather than arithmetic mean, values were used in Figures 7·2 and 7·3 for the reasons given in section 7·3·1.)

Figure 7·2

Graphs of monthly median concentrations (ng m^{-3}) of cadmium, copper, lead and zinc in the air at sites 1 and 2 (derived from the data in Appendix 7·5). Note: site 1 values are for the period June 1987–May 1988, and site 2 values are for the period June 1988–January 1989.



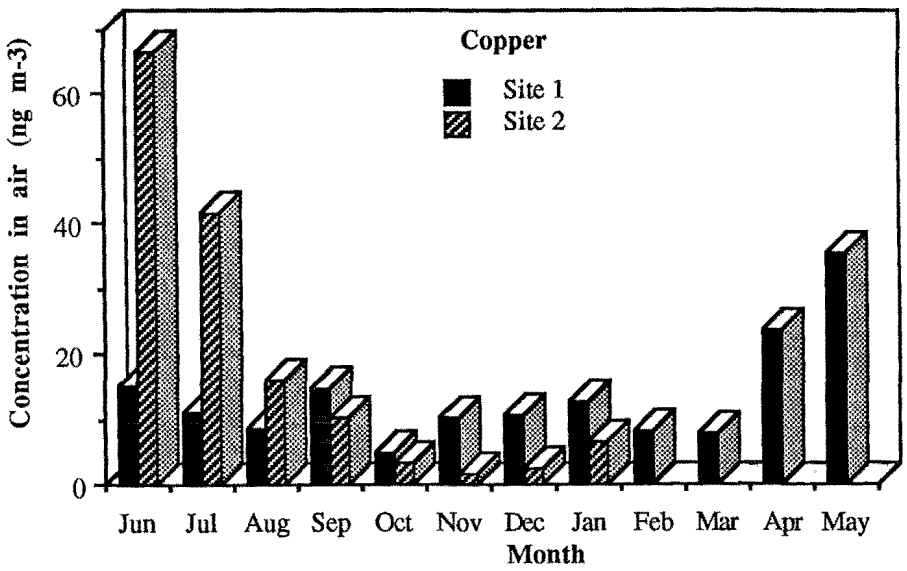
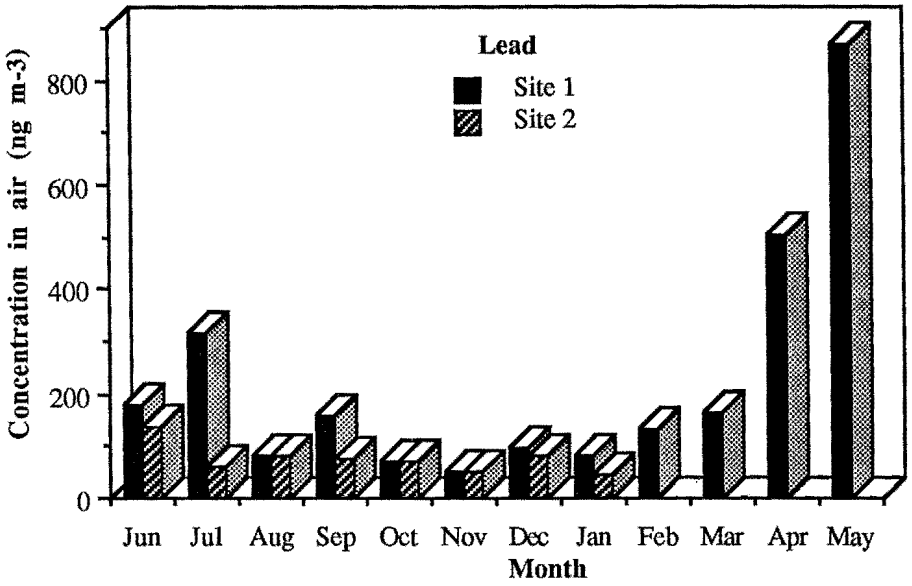


Figure 7·2 continued...



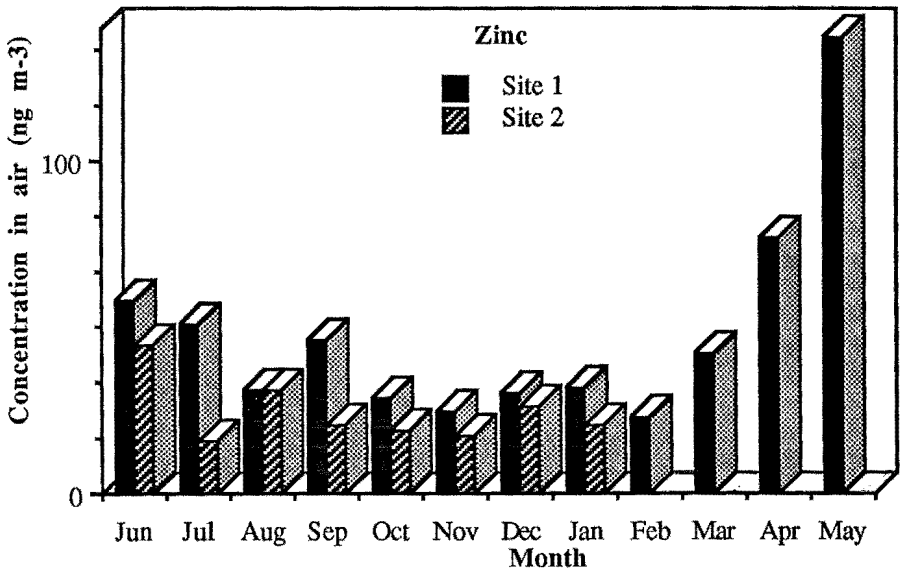
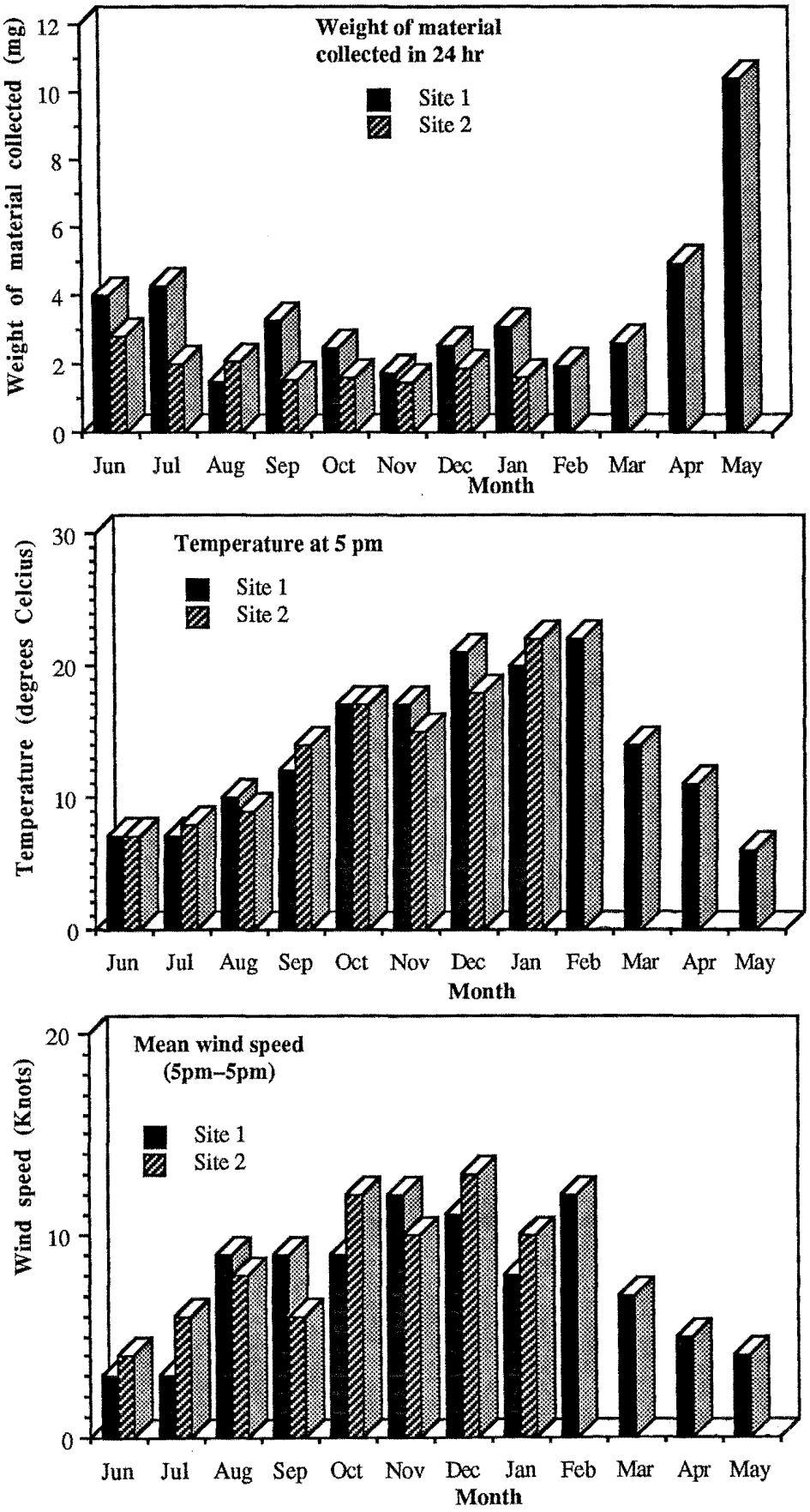


Figure 7·3

Graphs of monthly median values of the weight of material (mg) collected per 24 hr, the air temperature at 5pm, and the mean wind speed (5pm–5pm) at sites 1 and 2 (derived from the data in Appendix 7·5). Note: site 1 values are for the period June 1987–May 1988, and site 2 values are for June 1988–January 1989.



It can be seen by comparison of Figure 7·2 with Figure 7·3 that the highest ambient concentrations of cadmium, copper, lead and zinc (ng m^{-3}) at site 1 occur during those months characterized by the lowest temperatures and the lowest wind speeds; namely, from March (or April in some cases) to September. The weight of material collected per 24 hr sampling period (mg) (at site 1) is also the highest during these months (Figure 7·4). Metal concentrations in the air are lowest during the warmer (and windier) months October to February (Figures 7·2 and 7·3). There are two probable reasons why metal concentrations are highest in the months March to September:

1. increased use of home fireplaces during the coldest months,
2. the ability of the winter-time thermal-inversion layer to trap pollutants (both those from home fireplaces and those from other sources, such as lead from petrol lead) (section 7·1).

Relative enrichments of the metals in the air at site 1 during March to September can be estimated by division of the mean concentration of each metal for these months with the mean concentration of that metal during October to February. These values are given in Table 7·4.

Table 7·4

Estimation of relative enrichments of cadmium, copper, lead and zinc in the air at site 1 during the months March to September.

Metal	Mean concn. [March–Sept] (ng m^{-3})	Mean concn. [Oct–Feb] (ng m^{-3})	Relative enrichment during March–September[a]
Cadmium	1.20	0.345	3.48
Copper	41.7	11.4	3.66
Lead	333	92.3	3.60
Zinc	103	33.8	3.05

Note: **a.** Mean [March–September] / mean [October–February].

Two observations can be made from the data in Table 7·4. Firstly, there was on average over three times more cadmium, copper, lead and zinc (ng m^{-3}) in the air at site 1 during the months March to September than was the case for the months October to February. Secondly, the actual values of the four metals' enrichment factors in the air at site 1 during March to September are similar (mean value 3.45, standard deviation 0.28). This suggests that the additional amounts of cadmium, copper, lead and zinc released to Christchurch air during the coldest and least windy months may be derived from the same source (or sources), and/or are all influenced by the same concentration process(es). As mentioned above, one source of all four metals (which is operational during the coldest months) is likely to be combustion in home fireplaces; the concentration process (when

operative) is likely to be pollutant entrapment by thermal-inversion layers. The amount of material (mg) collected each 24 hr period at site 1 during the months March to September was 1.8 times higher than the corresponding figure for October to February.

Monthly variations in the ambient concentrations of cadmium, lead and zinc in samples collected from site 2 are similar to concentration variations in samples collected from site 1 during the same months in the preceding year (Figure 7·2 and Appendix 7·5). This "consistency between years" is most evident in the case of cadmium. The correlation coefficient between the mean cadmium concentrations for the same months of the different years (n = 8 pairs) falls into the "just significant" category ($R = 0.783$, $p<0.05$). This suggests that the predominant source(s) of cadmium at the two sites are characterized by the similar monthly output variations. Once again, this idea is consistent with the concept that combustion in home fireplaces is responsible for a large part of the seasonal variation in cadmium concentrations in Christchurch air. The comparatively high ambient concentrations of copper during June 1988–September 1988 (site 2) (Figure 7·2) may be the result of some of the samples having been "partially" contaminated with copper; that is, contaminated enough to have an undue influence on the median copper concentrations, but insufficiently contaminated to justify their being designated as outliers (section 7·3·1).

Monthly variations in the particulate concentrations ($\mu g\ g^{-1}$) of cadmium, copper, lead and zinc are illustrated in Figure 7·4, which is derived from the data in Appendix 7·5.

Figure 7·4

Graphs of monthly median concentrations ($\mu g\ g^{-1}$) of cadmium, copper, lead and zinc in the airborne particulates from sites 1 and 2 (derived from the data in Appendix 7·5). Note: site 1 values are for the period June 1987–May 1988, and site 2 values are for June 1988–January 1989.

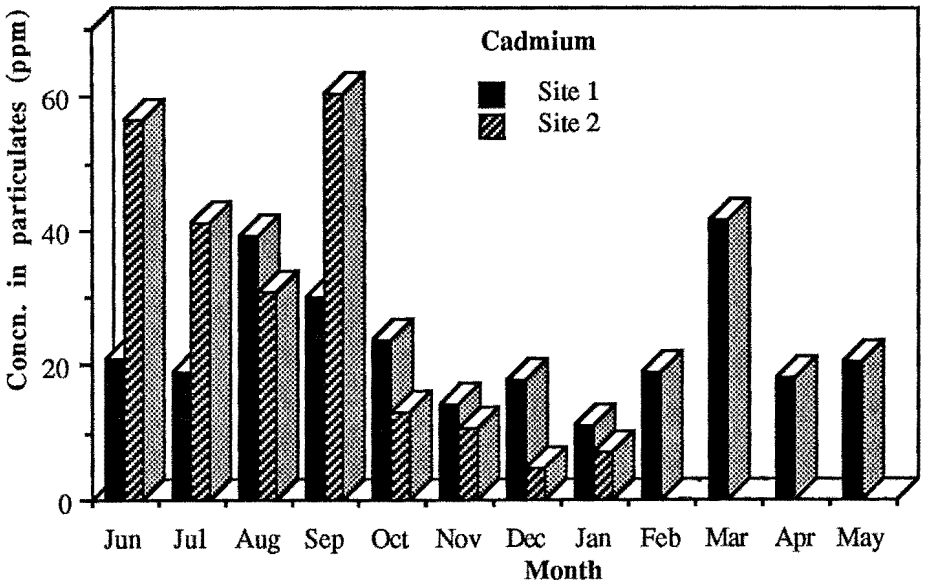
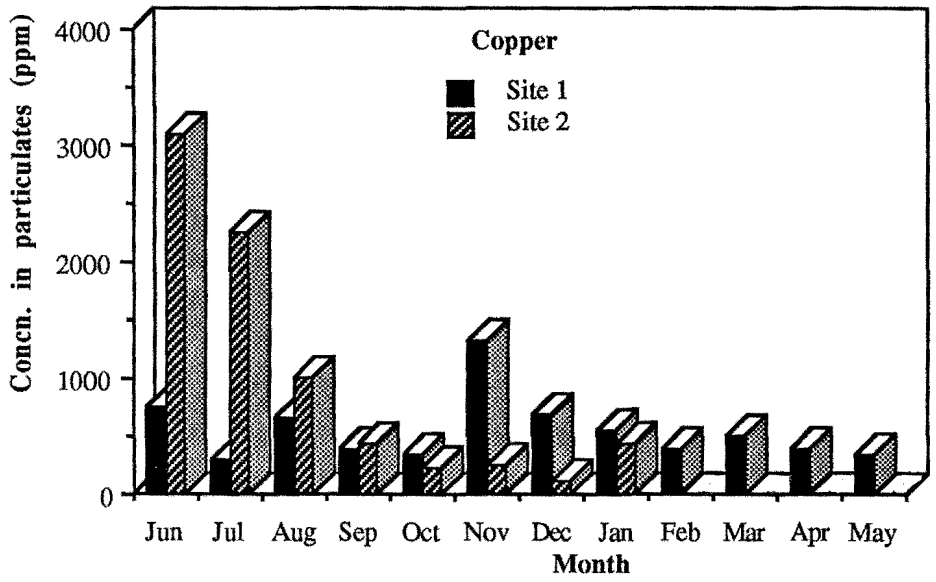
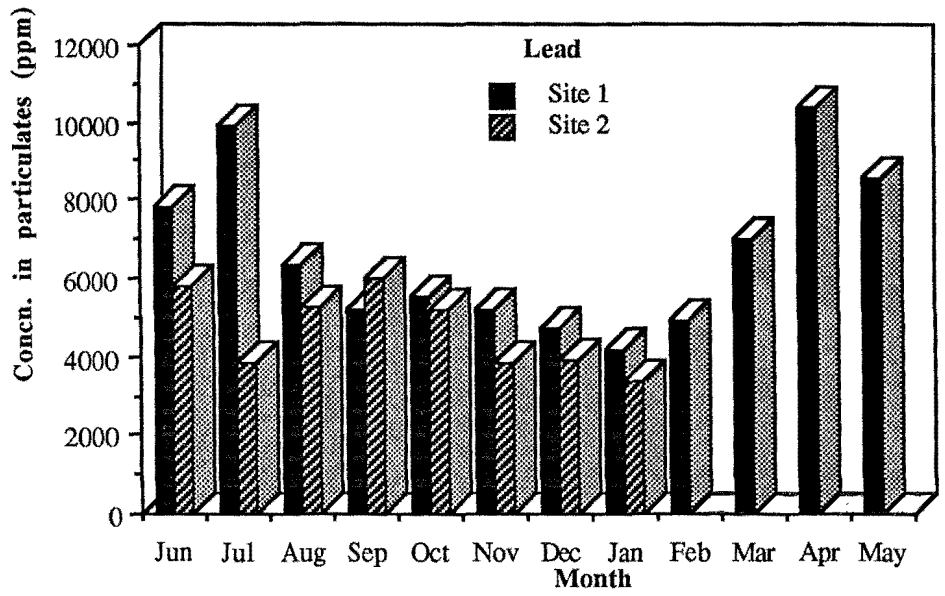
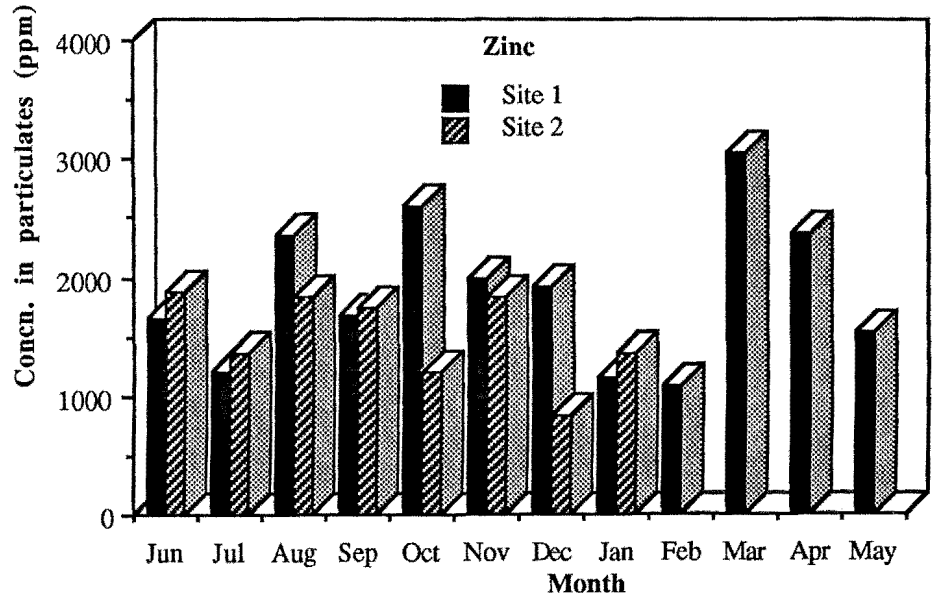


Figure 7·4 continued...







No clear trends are apparent in the graphs of cadmium, copper and zinc in Figure 7·4 which link the particulate concentrations of these metals ($\mu g\ g^{-1}$) with the time of year. Particulate concentrations of lead, however, follow the same general pattern as ambient lead concentrations, the highest being found during the months March to August and the lowest during September to February. This may imply that the source(s) of lead which come into operation during the cooler months is(are) producing lead-rich particles of finer diameter than those typically found in the air. However, the trend could also be a result of a greater fraction of (fine) lead-rich aerosols derived from petrol combustion being trapped by winter-time inversion layers.

7·3·3 Factors influencing cadmium, copper, lead and zinc concentrations in Christchurch air and airborne particulates

7·3·3a Correlations

Correlation coefficients for all the data except those relating to the variable "wind direction" were calculated. Metal concentrations ($ng\ m^{-3}$ and $\mu g\ g^{-1}$) and the values of the variable "weight of material collected in 24 hr" (mg) were approximately log-normal, and were therefore transformed to their natural logarithms prior to the derivation of the correlation matrices, which are given in Appendices 7·6 (site 1) and 7·7 (site 2). Correlation coefficients between the variable "wind direction" and other variables were not calculated, as they would have been meaningless (since a higher number in the direction scale of 0 to 360° does not represent a higher absolute wind direction). Correlations (everything more significant than $p<0.05$) between the site 1 variables ($n = 60$ pairs) are listed in Table 7·5; least-squares equations are given in cases where the correlation is highly significant. Correlations between site 2 variables ($n = 36$ pairs), and least-squares equations in the cases of those which are highly significant, are listed in Appendix 7·8. As an aid to visualization of interrelationships between variables, dendograms constructed from the correlation matrices are presented in Figure 7·5 (site 1) and Appendix 7·9 (site 2).

Table 7·5

Significant correlations present between concentrations of cadmium, copper, lead, zinc, the weight of material collected in 24 hr (mg) and meteorological parameters relating to site 1, and their degrees of significance. Least-squares equations are given in cases where the correlation is highly significant. (Number of data pairs = 60).

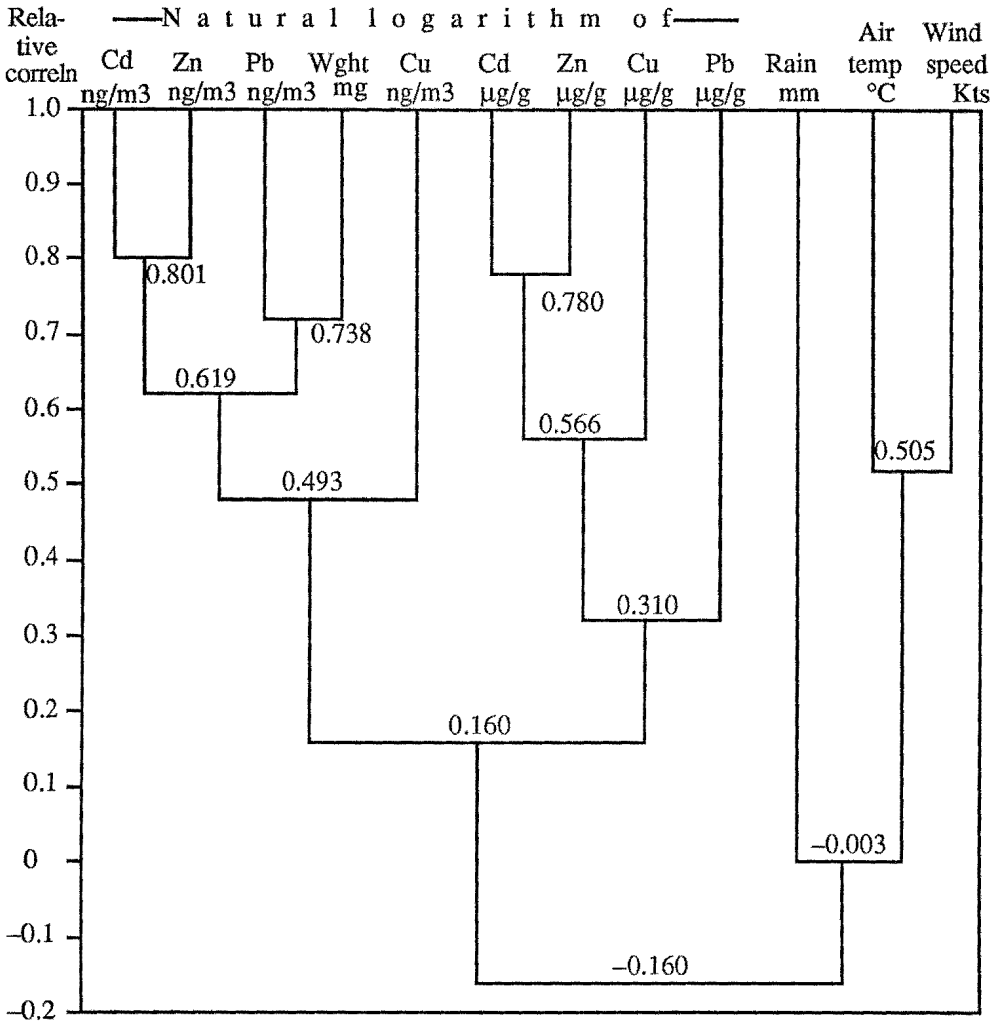
Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[ngCd m^{-3}] with...				
ln[ngCu m^{-3}]	0.563	<0.001	Highly	ln[ngCd m^{-3}] = 0.72ln[ngCu m^{-3}]–2.48
ln[ngPb m^{-3}]	0.705	<0.001	Highly	ln[ngCd m^{-3}] = 0.74ln[ngPb m^{-3}]–4.41
ln[ngZn m^{-3}]	0.801	<0.001	Highly	ln[ngCd m^{-3}] = 0.90ln[ngZn m^{-3}]–4.13
ln[µgCd g^{-1}]	0.588	<0.001	Highly	ln[ngCd m^{-3}] = 0.64ln[µgCd g^{-1}]–2.63
ln[µgPb g^{-1}]	0.431	<0.001	Highly	ln[ngCd m^{-3}] = 0.75ln[µgPb g^{-1}]–7.26

Table 7·5 continued...

Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[ngCd m^{-3}] with...				
ln[µgZn g^{-1}]	0.393	<0.01	Very	
ln[Weight (mg)]	0.502	<0.001	Highly	ln[ngCd m^{-3}] = 0.63ln[mg]–1.32
Air temperature (°C)	–0.461	<0.001	Highly	ln[ngCd m^{-3}] = 0.38–0.08[Air temp (°C)]
Mean wind speed (Kts)	–0.567	<0.001	Highly	ln[ngCd m^{-3}] = 0.44–0.14[Wind spd (Kts)]
ln[ngCu m^{-3}] with...				
ln[ngPb m^{-3}]	0.424	<0.001	Highly	ln[ngCu m^{-3}] = 0.35ln[ngPb m^{-3}]+0.76
ln[ngZn m^{-3}]	0.628	<0.001	Highly	ln[ngCu m^{-3}] = 0.55ln[ngZn m^{-3}]+0.39
ln[µgCu g^{-1}]	0.403	<0.01	Very	
ln[Weight (mg)]	0.353	<0.01	Very	
Air temperature (°C)	–0.298	<0.02	Quite	
Mean wind speed (Kts)	–0.255	<0.05	Just	
ln[ngPb m^{-3}] with...				
ln[ngZn m^{-3}]	0.710	<0.001	Highly	ln[ngPb m^{-3}] = 0.76ln[ngZn m^{-3}]+2.12
ln[µgCu g^{-1}]	–0.406	<0.01	Very	
ln[µgPb g^{-1}]	0.538	<0.001	Highly	ln[ngPb m^{-3}] = 0.89ln[µgPb g^{-1}]–2.78
ln[Weight (mg)]	0.738	<0.001	Highly	ln[ngPb m^{-3}] = 0.87ln[mg]+4.13
Air temperature (°C)	–0.596	<0.001	Highly	ln[ngCd m^{-3}] = 6.32–0.10[Air temp (°C)]
Mean wind speed (Kts)	–0.637	<0.001	Highly	ln[ngCd m^{-3}] = 6.22–0.15[Wind spd (Kts)]
ln[ngZn m^{-3}] with...				
ln[µgCd g^{-1}]	0.408	<0.01	Very	
ln[µgPb g^{-1}]	0.356	<0.01	Very	
ln[µgZn g^{-1}]	0.554	<0.001	Highly	ln[ngZn m^{-3}] = 0.62ln[µgZn g^{-1}]–0.83
ln[Weight (mg)]	0.555	<0.001	Highly	ln[ngZn m^{-3}] = 0.62ln[mg]+3.20
Air temperature (°C)	–0.465	<0.001	Highly	ln[ngZn m^{-3}] = 4.79–0.07[Air temp (°C)]
Mean wind speed (Kts)	–0.489	<0.001	Highly	ln[ngZn m^{-3}] = 4.70–0.11[Wind spd (Kts)]
ln[µgCd g^{-1}] with...				
ln[µgCu g^{-1}]	0.556	<0.001	Highly	ln[µgCd g^{-1}] = 0.66ln[µgCu g^{-1}]–1.03
ln[µgPb g^{-1}]	0.533	<0.001	Highly	ln[µgCd g^{-1}] = 0.86ln[µgPb g^{-1}]–4.44
ln[µgZn g^{-1}]	0.780	<0.001	Highly	ln[µgCd g^{-1}] = 0.90ln[µgZn g^{-1}]-3.76
ln[Weight (mg)]	–0.256	<0.05	Just	
ln[µgCu g^{-1}] with...				
ln[µgZn g^{-1}]	0.576	<0.001	Highly	ln[µgCu g^{-1}] = 0.56ln[µgZn g^{-1}]+1.96
ln[Weight (mg)]	–0.594	<0.001	Highly	ln[µgCu g^{-1}] = 6.80–0.57ln[mg]
Mean wind speed (Kts)	0.327	<0.02	Quite	
ln[µgPb g^{-1}] with...				
ln[µgZn g^{-1}]	0.484	<0.001	Highly	ln[µgPb g^{-1}] = 0.35ln[µgZn g^{-1}]+6.12
Air temperature (°C)	–0.401	<0.01	Very	
Mean wind speed (Kts)	–0.339	<0.01	Very	
ln[µgZn g^{-1}] with...				
ln[Weight (mg)]	–0.289	<0.05	Just	
ln[Weight (mg)] with...				
Air temperature (°C)	–0.388	<0.01	Very	
Mean wind speed (Kts)	–0.545	<0.001	Highly	ln[Wght(mg)] = 1.90–0.011[Wind spd (Kts)]
Air temp (°C) with...				
Mean wind speed (Kts)	0.505	<0.001	Highly	Air temp (°C) = 0.73[Wind spd (Kts)]+7.56

Figure 7·5

Dendogram showing relative interrelationships between variables in the site 1 data set. ("Wght" refers to the weight of material collected in 24 hr (mg).)

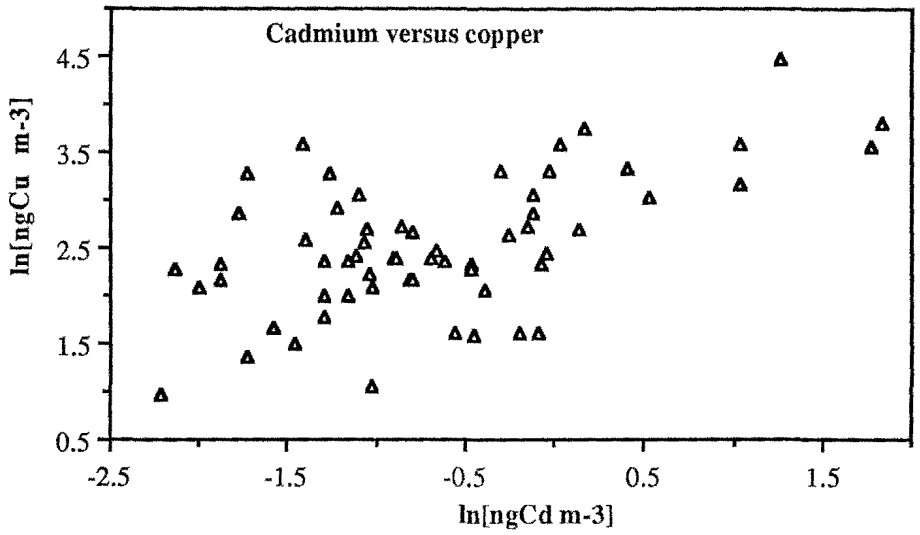


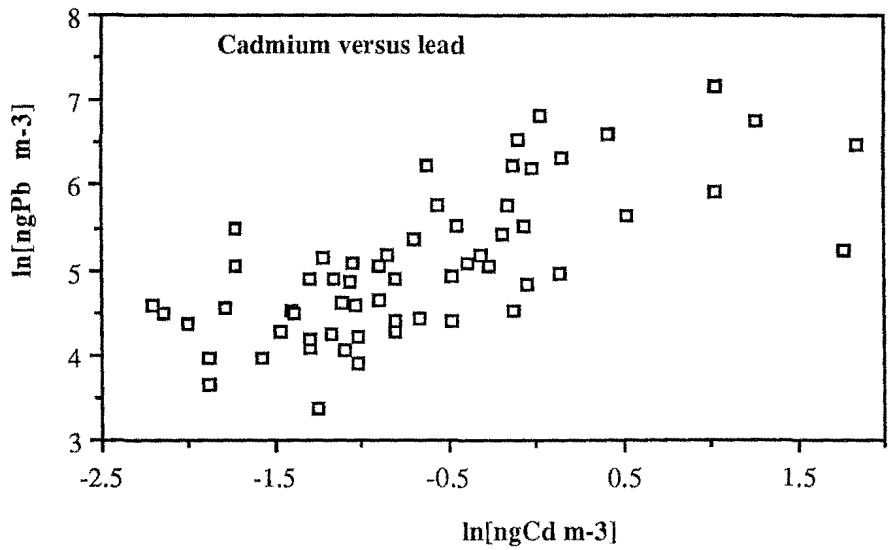
The following observations can be made from the data in Table 7·5 and Appendices 7·6–7·8:

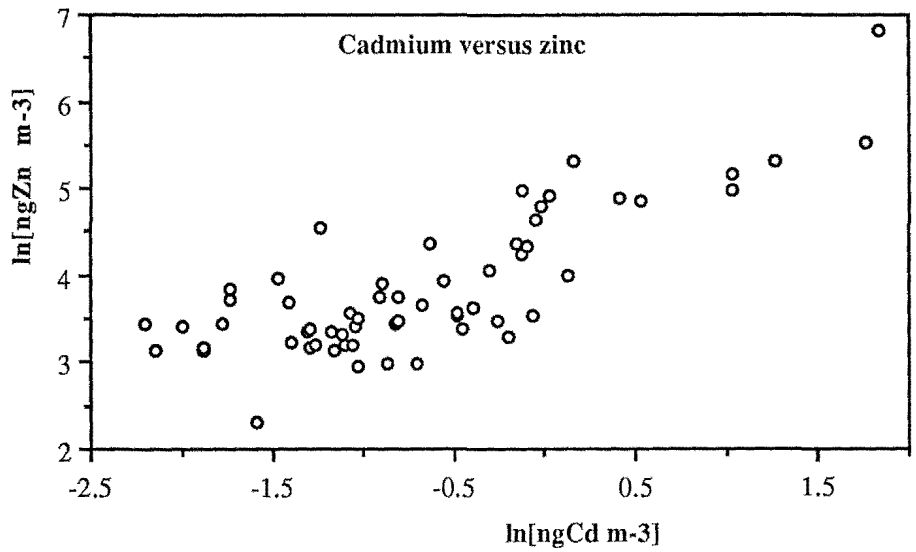
1. Metal concentrations in the air (ng m^{-3}) are all highly intercorrelated in the site 1 data. Among other things, this could suggest that sources of copper, lead and zinc to Christchurch air are also likely to be sources of cadmium. All ambient metal concentrations except for the pair copper–lead are correlated in the site 2 data set. The fact that the copper and lead concentrations in the air are uncorrelated in the site 2 data may suggest that the predominant source of these two metals at that site differ. At site 1 a major source of lead is likely to be the combustion of petrol lead in cars (section 7·3·1). This could also be a source of copper (Chapter 4), which would give rise to the observed correlation between the two metals at that location. Scattergrams illustrating the relationships between ambient concentrations of cadmium and copper, cadmium and lead, and cadmium and zinc at site 1 are presented in Figure 7·6.

Figure 7·6

Scattergrams showing the relationships between concentrations of cadmium (ng m^{-3}) in air at site 1 and those of copper, lead and zinc (least-squares equations are given in Table 7·5).



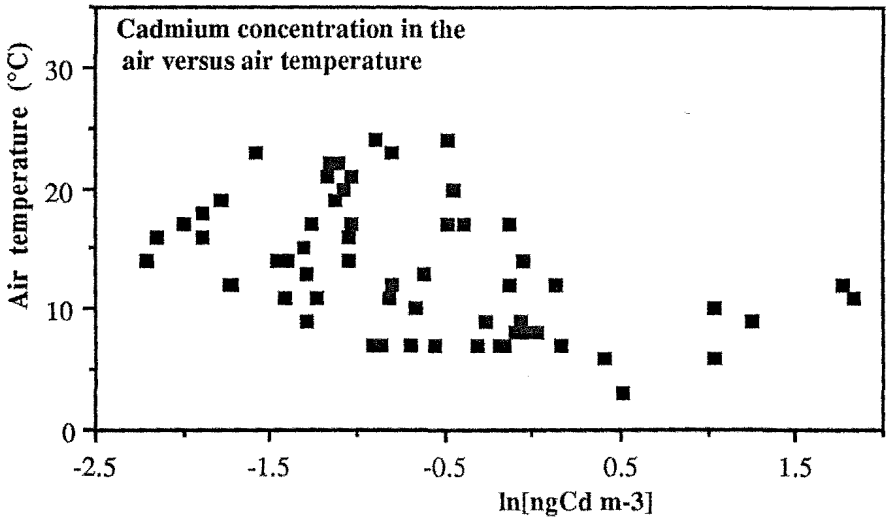


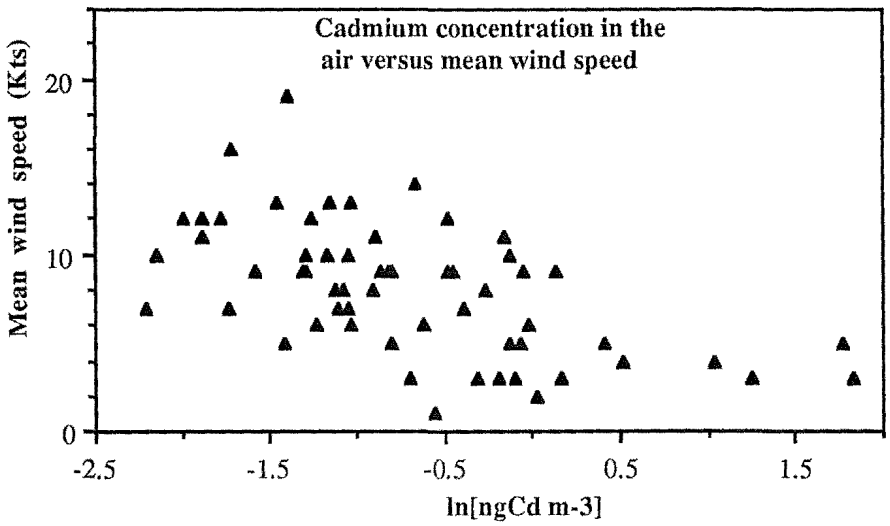


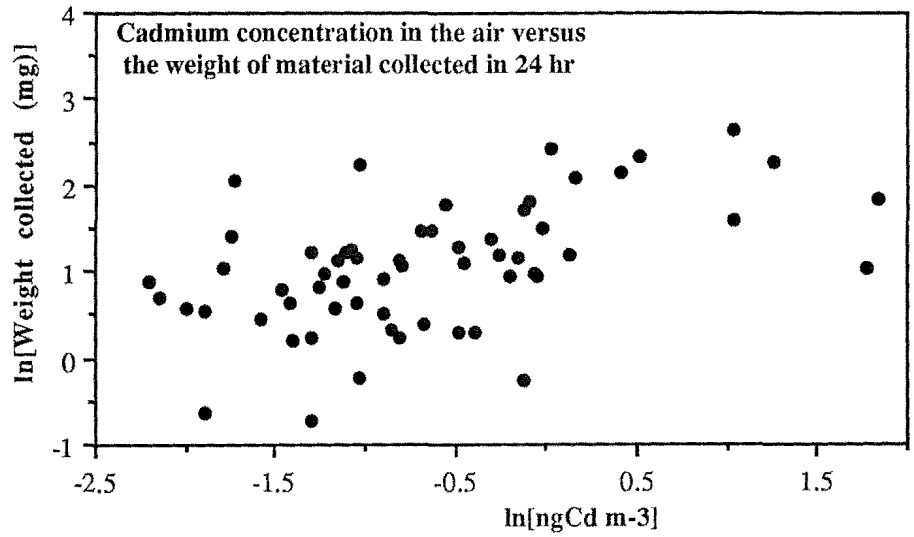
2. Metal concentrations (ng m^{-3}) in the air at both sites show strong negative correlations with air temperature (°C) and mean wind speed (Kts), which are themselves highly correlated. These relationships have already been inferred from graphs in section 7·3·2. The weight of material collected in 24 hr (mg) is also negatively correlated to air temperature and mean wind speed at site 1, but not at site 2. Additionally, in the site 1 data, the weight of material collected is also strongly related to the concentration (ng m^{-3}) of each metal in the air (in the site 2 data, only ln[ngPb m^{-3}] shows this relationship). These correlations probably reflect the ability of the winter-time thermal-inversions which occur above site 1 to concentrate airborne pollutants. Scattergrams showing the relationships between cadmium concentrations (ng m^{-3}) and air temperature, mean wind speed, and the weight of material collected in 24 hr (mg) at site 1 are given in Figure 7·7.
3. Rainfall (mm) has weak negative correlations with the ambient metal concentrations (ng m^{-3}), the strongest of which (lead and zinc concentrations at site 2) fall into the "just significant" category. However, it is likely that the mathematical relationship between rainfall and the metal concentrations is somewhat weakened by the high frequency of "zero" observations, as it only rained on 20 of the 60 sampling days at site 1, and on 8 of the 36 sampling days (with outliers removed) at site 2.
4. Particulate concentrations (μg g^{-1}) of all the metal pairs except copper and lead are strongly intercorrelated in both sites' data sets. Once again, this suggests that sources of copper, lead or zinc are also likely to be sources of cadmium. A possible reason for the lack of a correlation between particulate concentrations of copper and lead at both sites could be that the predominant sources of the two metals at both sites produce different sized particles. For example, traffic may constitute an important source of copper and lead at site 1 (see above). Copper-rich particles derived from car radiators are likely to have a different size distribution to lead-rich particles derived from petrol lead.
5. Correlations between metal particulate concentrations (μg g^{-1}) and the weight of material collected in 24 hr (mg) imply that the former tend to decrease as the latter increases. This seems to imply that the concentrations of metals in particles added (temporarily) to the Christchurch atmosphere are actually lower than the concentrations in "naturally-airborne" particles. This seems intuitively reasonable, as the finest (metal-rich) particles would stay airborne for the longest time. (It has already been mentioned that particulate concentrations of metals are higher in rural areas than they are in urban areas (section 7·3·1).)
6. In the site 1 data, particulate lead concentrations (μg g^{-1}) are negatively correlated with air temperature and wind speed, whereas in the site 2 data, they are not. Conversely, in the site 2 data, cadmium and copper particulate concentrations are negatively correlated with air temperature and wind speed, whereas in the site 1 data, they are not. These relationships are interesting, but difficult to interpret without more data.

Figure 7·7

Scattergrams showing the relationships between cadmium concentrations (ng m^{-3}) in the air at site 1 and air temperature (°C), mean wind speed (Kts), and the weight of material collected in 24 hr (mg).







To assess the effect of wind direction on cadmium levels (ng m^{-3}), cadmium data was classified according to the various wind directions. Mean cadmium concentrations, standard deviations and 95% confidence intervals for each wind direction (at both sites) are given in Table 7·6.

Table 7·6

Mean cadmium concentrations, standard deviations and 95% confidence intervals for each wind direction.

Wind direction	Number in sample	Mean Cd concn (ng m^{-3})	Standard devn	95% error on mean[a]
Site 1				
NE	12	0.93	1.61	±0.91
SW	9	1.02	0.73	±0.48
E	8	0.37	0.25	±0.18
ENE	6	0.35	0.20	±0.18
NW	6	0.59	0.55	±0.50
W	4	3.31	2.3	±4.5
E/SW	4	0.33	0.09	±0.17
SW/NE	3	0.70	0.31	±0.6
NW/SW	2	0.29	0.16	±1.03
N	1	0.33		
E/S	1	0.96		
NW/NE	1	0.88		
Site 2				
NW	8	0.63	0.50	±0.36
ENE	7	0.24	0.21	±0.17
E	6	0.57	0.67	±0.60
SSW	4	0.34	0.21	±0.28
NE	3	0.60	0.20	±0.42
SW	3	1.19	0.64	±1.32
NNW	3	0.19	0.12	±0.24
S	3	0.15	0.17	±0.35
WNW	2	0.34	0.25	±1.58
SSE	1	0.185		

Note: **a.** Student's t-test.

It can be seen from the data in Table 7·6 that cadmium concentrations for any given wind direction are not statistically higher than they are for the remaining wind directions (all the confidence intervals overlap). However, it should be noted that due to the small number of observations in each wind direction category, the confidence interval errors on the mean cadmium concentrations are large. The data in Table 7·6 does not eliminate the possibility that wind direction can influence ambient cadmium concentrations.

7·3·3b Principal Components Analysis

The technique of Principal Components Analysis is described in section 4·3·3f. A PCA on the data relating to both sites was carried using a standard statistical software package ("Statview", Apple MacIntosh). In this study, all the variables except "wind direction" are continuous in nature (rather than discrete), and were entered into the computer

as their actual values (rather than as binary digits). The variable "wind direction" was excluded from the calculation. The results of the PCA on the site 1 and site 2 data sets are given in Table 7·7 and Appendix 7·10, respectively. In the case of the PCA on the site 2 data, variables relating to copper (ngCu m^{-3} and μgCu g^{-1}) were excluded from the calculation (in order to overcome difficulties associated with outliers).

Table 7·7

Factor score weights of the oblique transformation solution (Orthotran/Varimax) of the Principal Components Analysis of the site 1 airborne particulates data.

Variable	Factor 1	Factor 2	Factor 3
ngCd m^{-3}	0.124	0.191	–0.146
ngCu m^{-3}	0.151	0.245	–0.136
ngPb m^{-3}	0.245	-0.029	0.045
ngZn m^{-3}	0.107	0.190	–0.158
μgCd g^{-1}	–0.045	0.268	–0.009
μgCu g^{-1}	–0.134	0.218	0.185
μgPb g^{-1}	0.063	0.088	0.382
μgZn g^{-1}	–0.050	0.282	0.021
Wght/24 hr (mg)	0.248	–0.082	–0.045
Rainfall (mm)	–0.011	–0.036	0.579
Air temp (°C)	–0.205	0.106	–0.394
Mn wind spd (Kts)	–0.188	0.161	–0.072
Proportionate variance contributions (%)	47	37	16

Three factors emerged from the 12 site 1 variables and from the 10 remaining site 2 variables (Table 7·7 and Appendix 7·10). The first factor has (relatively) high positive scores in the rows corresponding to the concentrations of the metals in the air (ng m^{-3}) and the weight of material collected in 24 hr (mg), and high negative scores in the "air temperature" and "mean wind speed" rows. These associations imply that as the air temperature and mean wind speed decrease, the amount of material in the air and the ambient metal concentrations (ng m^{-3}) increase. The existence of these relationships has already been inferred from the data in sections 7·3·2 and 7·3·3a.

The second factor of the PCA results derived from the site 1 data has high positive scores in almost all the rows corresponding to metal concentrations (both ng m^{-3} and μg g^{-1}) (Table 7·7). In the case of the PCA of site 2 data, the second factor has the highest positive scores in the rows corresponding to metal concentrations in particulates (μg g^{-1}) (Appendix 7·10). It is likely that this second factor represents the "bigness" of the metal concentration variables themselves (Jollife, 1986).

In the results of the PCA on the site 1 data, the highest positive and negative scores of the third factor are in the "rainfall" and "air temperature" rows, respectively. Negative scores are also apparent in the rows corresponding with ambient concentrations (ng m^{-3}) of cadmium, copper, and zinc; whereas those representing the particulate concentrations ($\mu g\ g^{-1}$) of copper and lead have positive scores. Thus, at site 1 it could be expected that as rainfall increases (and/or as the air temperature decreases), the concentrations of cadmium, copper and zinc in the air decrease, whereas the concentrations of copper and lead in particulates increase. In terms of the effect of rainfall, this interpretation of the factor three data seems reasonable. Mild negative correlations between rainfall and the metal concentrations in the air were mentioned in section 7·3·3a. It could also be envisaged that rainfall may preferentially remove the larger airborne particulates, causing selective enrichment of the finer (metal-rich) particulates (and a corresponding increase in particulate metal concentrations). However, it has already been seen that a fall in the air temperature causes the ambient concentrations of the metals to increase, not to decrease (above, section 7·3·2, section 7·3·2a), which implies that the above interpretation relating to factor three is incorrect. Additionally, factor three has opposite scores in the "rainfall" and "air temperature" rows in the PCA of the site 1 data than it has in the PCA of site 2 data (Table 7·7 and Appendix 7·10). As has been mentioned in section 4·3·3f, PCA should be viewed as only an approximation to reality (Gorsuch, 1983).

7·4 Conclusion

Samples of airborne particulates were collected at two Christchurch sites. At site 1, in the suburb of Avonside, five 24 hr samples were collected each month for a total of 12 months; and at site 2, in the suburb of Huntsbury, five 24 hr samples were collected each month for a total of eight months.

The geometric mean concentrations of cadmium in the air at the two sites are 0.516 ng m^{-3} (site 1) and 0.305 ng m^{-3} (site 2) (range over both sites 0.043–6.29 ng m^{-3}). Absorption of cadmium by Christchurch residents from inhaled airborne particulates could fall in the range 0.83–1.65 $\mu g\ year^{-1}$, which represents only 0.17–0.35% of the amount of cadmium estimated (in Chapter 6) to be absorbed by Christchurch residents from food sources. Arithmetic mean concentrations of cadmium in Christchurch air are similar to (arithmetic mean) concentrations typically found in the world's rural areas.

Geometric mean concentrations of cadmium in the airborne particulates at sites 1 and 2 are 21.6 $\mu g\ g^{-1}$ and 20.4 $\mu g\ g^{-1}$, respectively. Arithmetic mean concentrations are slightly higher than (arithmetic mean) values reported for urban areas of the U.S.A., possibly because fewer anthropogenic "particle-dispersal" processes are operative in Christchurch than in most North American urban areas.

Concentrations of lead and zinc (ng m^{-3}) and the weight of collectable material (mg) in the air were found to be lower at site 2 than at site 1 during the same months of the previous year. Petrol lead and an unpainted galvanized-iron roof were thought to be the sources of extra lead and zinc at site 1. Additional concentrations of material in the air at site 1 are likely to be the result of winter-time thermal-inversion layers hindering the dispersal of pollutants at that site.

Comparison of the various variable's monthly means, correlation coefficients between variables and the results of Principal Components Analyses on the two sites' data sets all show that ambient concentrations of cadmium, copper, lead and zinc (ng m^{-3}) tend to increase with decreasing air temperature and mean wind speed. The mean concentration of each metal in the air at site 1 for the months characterized by the lowest air temperatures and mean wind speeds (March–September) is about 3.45 times higher than that metal's mean concentration for the other months. The probable reasons for the observed relationships are the increased use of household fires during the coldest months and the ability of the winter-time thermal-inversion layer to trap pollutants.

The effect of rainfall on the concentrations of cadmium, copper, lead and zinc in the air is not so noticeable, probably because no rain fell during the majority of sampling days (at both sites). Correlation coefficients between the variable "rainfall" and the ambient metal concentrations (ng m^{-3}) are in most cases weakly negative. No relationship was found to exist between cadmium concentrations in the air and the wind direction.

Strong correlations between concentrations of cadmium and those of the other three metals (ng m^{-3} and $\mu g\ g^{-1}$) suggest that sources of copper, lead and zinc to Christchurch air are also likely to be sources of cadmium.

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7·6 Appendices

Appendix 7·1 (section 7·3·1)

Complete set of data relating to the sampling of air particulates at site 1 in the suburb of Avonside.

Month and year: June 1987	Dates samples taken				
	22–23	23–24	24–25	25-26	26-27
Concentration in air (ng m^{-3})					
Cadmium	1.17	0.735	0.424	0.406	0.912
Copper	42	27	15	11	5
Lead	551	178	179	104	699
Zinc	203	58	20	42	75
Concentration in particulates (μg g^{-1})					
Cadmium	16.7	21.1	34.3	26.8	17.2
Copper	597	757	1 220	759	100
Lead	7 840	5 100	14 500	6 890	13 200
Zinc	2 890	1 660	1 640	2 750	1 410
Weight of matter collected in 24 hr (mg)	7.93	3.97	1.40	1.68	6.02
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	14.4	30.9	0.4
Air temperature (5pm) (°C)	7	7	7	7	8
Mean wind speed (5pm–5pm) (Kts)	3	3	9	8	3
Mean wind direction (5pm–5pm)	L+V[a]	L+V[a]	NE	E	E

Month and year: July 1987	Dates samples taken				
	22–23	23–24	24–25	25-26	26-27
Concentration in air (ng m^{-3})					
Cadmium	1.17	0.975	0.499	0.574	0.826
Copper	15	27	11	5	5
Lead	317	487	213	319	223
Zinc	78	120	20	51	27
Concentration in particulates (μg g^{-1})					
Cadmium	42.2	24.8	13.1	11.1	19.0
Copper	538	677	296	100	233
Lead	11 400	12 400	6 050	6 160	9 890
Zinc	2 810	3 060	532	987	1 200
Weight of matter collected in 24 hr (mg)	3.17	4.44	4.30	5.87	2.56
Climatological data					
Rainfall (5pm–5pm) (mm)	4.1	1.3	0	0.5	0
Air temperature (5pm) (°C)	7	8	7	7	7
Mean wind speed (5pm–5pm) (Kts)	11	6	3	1	3
Mean wind direction (5pm–5pm)	SW	SW	NE	E	SW/NE

Appendix 7·1 continued...

Month and year: August 1987	Dates samples taken				
	21–22	22–23	23–24	24-25	25-26
Concentration in air (ng m^{-3})					
Cadmium	0.274	0.931	0.274	0.513	0.444
Copper	7.36	10.2	5.96	11.7	8.65
Lead	133	249	66.2	82.9	71.0
Zinc	29.2	34.4	23.6	38.9	30.8
Concentration in particulates (µg g^{-1})					
Cadmium	9.06	39.0	63.3	39.2	34.0
Copper	241	428	1 380	895	662
Lead	4 390	10 500	15 300	6 330	5 420
Zinc	965	1 440	5 460	2 970	2 350
Weight of matter collected in 24 hr (mg)	3.42	2.69	0.49	1.48	1.27
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0.1	0.3	0.2
Air temperature (5pm) (°C)	13	9	9	10	11
Mean wind speed (5pm–5pm) (Kts)	10	5	9	14	9
Mean wind direction (5pm–5pm)	SW	SW/NE	ENE	NE	E

Month and year: September 1987	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.450	0.294	1.14	0.178	0.769
Copper	8.82	18.3	14.9	26.2	9.66
Lead	132	169	140	156	158
Zinc	42.5	94.6	53.5	46.2	32.7
Concentration in particulates (µg g^{-1})					
Cadmium	17.6	124	40.0	2.56	29.9
Copper	346	770	521	378	376
Lead	5 190	7 130	4 910	2 240	6 130
Zinc	1 670	3 980	1 870	667	1 270
Weight of matter collected in 24 hr (mg)	2.89	2.63	3.31	7.80	3.26
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0.4	0.4	0	0
Air temperature (5pm) (°C)	12	11	12	12	9
Mean wind speed (5pm–5pm) (Kts)	9	6	9	16	8
Mean wind direction (5pm–5pm)	E/SW	SW/E	SW	NW/SW	SW

Appendix 7·1 continued...

Month and year: October 1987	Dates samples taken				
	23–24	24–25	25–26	26-27	27-28
Concentration in air (ng m^{-3})					
Cadmium	0.328	0.639	0.359	0.272	0.231
Copper	11.1	4.91	2.88	10.7	4.53
Lead	99.6	246	66.4	60.2	72.4
Zinc	27.9	29.0	33.6	28.5	53.4
Concentration in particulates (µg g^{-1})					
Cadmium	15.2	23.7	43.1	24.8	11.4
Copper	512	182	346	980	224
Lead	4 610	9 110	7 980	5 500	3 590
Zinc	1 290	1 080	4 040	2 600	2 650
Weight of matter collected in 24 hr (mg)	2.44	3.02	9.40	1.25	2.23
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	0	0
Air temperature (5pm) (°C)	19	20	17	15	14
Mean wind speed (5pm–5pm) (Kts)	8	9	6	9	13
Mean wind direction (5pm–5pm)	N	SW	NE	NE	NE

Month and year: November 1987	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.152	0.284	0.135	0.881	0.152
Copper	8.68	26.5	7.98	21.5	10.4
Lead	39.1	28.9	78.7	91.3	53.0
Zinc	22.8	24.5	30.2	145	23.7
Concentration in particulates (µg g^{-1})					
Cadmium	10.2	14.2	8.88	133	31.3
Copper	585	1 320	526	3 260	2 130
Lead	2 630	1 440	5 180	13 800	10 900
Zinc	1 530	1 220	1 990	21 900	4 860
Weight of matter collected in 24 hr (mg)	1.71	2.25	1.76	0.76	0.54
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	5.0	0
Air temperature (5pm) (°C)	16	17	17	17	18
Mean wind speed (5pm–5pm) (Kts)					
Mean wind direction (5pm–5pm)	NE	E	E	SW	ENE

Appendix 7·1 continued...

Month and year: December 1987	Dates samples taken				
	17–18	18–19	19–20	20-21	21-22
Concentration in air (ng m^{-3})					
Cadmium	0.408	0.168	0.247	0.353	0.311
Copper	10.8	17.7	13.3	9.11	10.6
Lead	156	94.1	90.0	96.6	70.6
Zinc	49.4	31.4	25.3	30.4	28.5
Concentration in particulates (µg g^{-1})					
Cadmium	17.6	6.58	20.7	12.6	20.8
Copper	466	693	1 120	325	708
Lead	6 750	3 680	7 540	3 440	4 720
Zinc	2 130	1 230	2 120	1 080	1 910
Weight of matter collected in 24 hr (mg)	2.52	2.85	1.21	3.23	1.80
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	5.6	0	3.4
Air temperature (5pm) (°C)	24	19	14	16	21
Mean wind speed (5pm–5pm) (Kts)	11	12	19	10	10
Mean wind direction (5pm–5pm)	NW/SW	E	SW/E	ENE	E/SW

Month and year: January 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.622	0.117	0.343	0.333	0.448
Copper	10.4	9.81	12.8	21.5	14.3
Lead	80.4	88.0	129	57.7	81.8
Zinc	34.1	22.8	34.9	24.4	31.9
Concentration in particulates (µg g^{-1})					
Cadmium	52.3	6.56	11.0	11.1	16.3
Copper	870	550	412	717	523
Lead	6 760	4 560	4 150	1 920	2 980
Zinc	2 870	1 280	1 120	814	1 160
Weight of matter collected in 24 hr (mg)	1.35	2.00	3.46	3.38	3.06
Climatological data					
Rainfall (5pm–5pm) (mm)	1.2	0	0	0	0
Air temperature (5pm) (°C)	17	16	20	22	23
Mean wind speed (5pm–5pm) (Kts)	9	10	8	7	5
Mean wind direction (5pm–5pm)	W	NE	NE/SW	E	ENE

Appendix 7·1 continued...

Month and year: February 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.206	0.350	0.315	0.622	0.358
Copper	5.34	14.7	7.30	9.68	8.13
Lead	52.3	163	133	138	50.2
Zinc	10.0	24.5	23.2	35.7	19.2
Concentration in particulates (µg g^{-1})					
Cadmium	14.8	20.6	11.6	19.0	52.3
Copper	385	864	269	295	1 190
Lead	3 770	9 620	4 890	4 210	7 340
Zinc	721	1 440	855	1 090	2 810
Weight of matter collected in 24 hr (mg)	1.56	1.91	3.07	3.56	0.80
Climatological data					
Rainfall (5pm–5pm) (mm)	7.4	1.9	0	0	10.3
Air temperature (5pm) (°C)	23	14	22	24	21
Mean wind speed (5pm–5pm) (Kts)	9	7	13	12	13
Mean wind direction (5pm–5pm)	NW	NW	NW	NW	NW

Month and year: March 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.176	0.957	5.87	0.110	0.675
Copper	3.94	11.6	34.8	2.64	7.72
Lead	239	125	188	97.0	161
Zinc	41.8	104	248	31.0	37.5
Concentration in particulates (µg g^{-1})					
Cadmium	5.17	41.7	235	5.23	56.9
Copper	116	504	1 400	126	630
Lead	6 990	5 420	7 550	4 620	13 100
Zinc	1 220	4 540	9 940	1 480	3 060
Weight of matter collected in 24 hr (mg)	4.11	2.58	2.83	2.39	1.35
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	0	1.1
Air temperature (5pm) (°C)	12	14	12	14	17
Mean wind speed (5pm–5pm) (Kts)	7	9	5	7	7
Mean wind direction (5pm–5pm)	ENE	E/S	NE	NE	ENE

Appendix 7·1 continued...

Month and year: April 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	2.80	6.29	0.537	0.882	0.244
Copper	23.9	44.7	10.5	17.4	35.5
Lead	372	652	508	501	91.5
Zinc	175	903	77.3	68.7	39.4
Concentration in particulates (μg g^{-1})					
Cadmium	66.8	109	13.7	18.3	14.8
Copper	571	772	268	361	384
Lead	8 880	11 300	12 900	10 400	5 540
Zinc	8 950	15 600	1 970	1 420	2 380
Weight of matter collected in 24 hr (mg)	4.90	6.35	4.39	5.54	1.86
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	0	0
Air temperature (5pm) (°C)	10	11	13	12	11
Mean wind speed (5pm–5pm) (Kts)	4	3	6	5	5
Mean wind direction (5pm–5pm)	SW	W	SW	NW/NE	E

Month and year: May 1988	Dates samples taken				
	23–24	24–25	25–26	26-27	27-28
Concentration in air (ng m^{-3})					
Cadmium	1.68	2.80	1.03	3.51	1.51
Copper	20.6	35.7	36.3	87.7	28.2
Lead	280	1 280	926	872	731
Zinc	127	143	138	206	133
Concentration in particulates (μg g^{-1})					
Cadmium	20.4	22.6	9.35	34.3	17.8
Copper	250	287	330	444	334
Lead	3 400	10 300	8 400	8 530	8 650
Zinc	1 540	1 150	1 260	2 020	1 570
Weight of matter collected in 24 hr (mg)	10.4	14.0	11.2	9.68	8.69
Climatological data					
Rainfall (5pm–5pm) (mm)	6.0	0	0	0	0
Air temperature (5pm) (°C)	3	6	8	9	6
Mean wind speed (5pm–5pm) (Kts)	4	4	2	3	5
Mean wind direction (5pm–5pm)	NW	W	NE	W	NE

Note: **a.** "L+V" = "light and variable".

Appendix 7·2 (section 7·3·1)

Complete set of data relating to the sampling of air particulates at site 2 in the suburb of Huntsbury.

Month and year: June 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.744	1.80	1.03	0.615	0.507
Copper	338	66.9	41.1	136	148
Lead	139	184	82.9	33.7	144
Zinc	44.3	77.0	22.1	19.3	46.1
Concentration in particulates (µg g^{-1})					
Cadmium	14.0	56.5	77.8	193	20.5
Copper	6 360	2 100	3 100	42 600	6 000
Lead	2 610	5 790	6 250	10 600	5 820
Zinc	832	2 420	1 660	6 060	1 870
Weight of matter collected in 24 hr (mg)	6.20	3.74	1.60	0.34	2.82
Climatological data					
Rainfall (5pm–5pm) (mm)	0.7	0	0.8	0	0
Air temperature (5pm) (°C)	5	7	8	7	10
Mean wind speed (5pm–5pm) (Kts)	3	2	6	6	4
Mean wind direction (5pm–5pm)	NE	E	SW	NW	NW

Month and year: July 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.636	0.644	0.652	0.306	0.517
Copper	27.5	188	56.3	5.31	221
Lead	104	51.0	60.5	52.1	85.1
Zinc	24.1	25.5	16.0	13.6	14.4
Concentration in particulates (µg g^{-1})					
Cadmium	22.3	35.7	41.1	49.2	49.0
Copper	966	10 400	3 550	853	20 900
Lead	3 650	2 830	3 820	8 360	8 070
Zinc	846	1 410	1 010	2 180	1 360
Weight of matter collected in 24 hr (mg)	3.45	1.98	3.04	0.67	1.19
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	3.4	0	0
Air temperature (5pm) (°C)	8	8	8	10	16
Mean wind speed (5pm–5pm) (Kts)	4	6	5	14	6
Mean wind direction (5pm–5pm)	SW	NE	ENE	NW	WNW

Appendix 7·2 continued...

Month and year: August 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.377	0.481	0.901	1.80	0.185
Copper	15.8	19.7	15.8	171	12.7
Lead	102	77.8	134	83.7	18.7
Zinc	15.1	37.0	30.7	64.8	9.92
Concentration in particulates (µg g^{-1})					
Cadmium	23.6	23.9	30.9	99.4	52.0
Copper	991	980	543	9 470	3 560
Lead	6 400	3 870	4 620	13 400	5 260
Zinc	944	1 840	1 060	3 580	2 790
Weight of matter collected in 24 hr (mg)	1.78	2.38	3.25	2.07	0.38
Climatological data					
Rainfall (5pm–5pm) (mm)	2.6	0	0	0	4.7
Air temperature (5pm) (°C)	6	9	9	13	8
Mean wind speed (5pm–5pm) (Kts)	9	5	8	6	14
Mean wind direction (5pm–5pm)	NE	SSW	E	NW	SSE

Month and year: September 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.695	0.563	1.89	0.283	0.203
Copper	11.8	2.70	8.31	737	15.6
Lead	74.4	56.1	163	78.5	70.6
Zinc	20.3	16.4	62.3	27.2	11.3
Concentration in particulates (µg g^{-1})					
Cadmium	32.9	60.4	71.4	67.2	15.5
Copper	561	289	314	175 000	1 190
Lead	3 530	6 010	6 150	18 700	5 410
Zinc	963	1 750	2 350	6 470	865
Weight of matter collected in 24 hr (mg)	2.41	1.73	1.56	1.56	1.48
Climatological data					
Rainfall (5pm–5pm) (mm)	0	3.0	0	0	0
Air temperature (5pm) (°C)	22	11	14	14	13
Mean wind speed (5pm–5pm) (Kts)	6	8	4	6	7
Mean wind direction (5pm–5pm)	NW	SSW	SW	E	ENE

Appendix 7·2 continued...

Month and year: October 1988	Dates samples taken				
	22–23	23–24	24–25	25-26	26-27
Concentration in air (ng m^{-3})					
Cadmium	0.196	0.464	0.488	0.188	0.173
Copper	4.35	3.08	1.97	22.0	2.21
Lead	56.8	49.5	71.1	74.4	105
Zinc	18.0	25.0	33.6	17.2	19.0
Concentration in particulates (µg g^{-1})					
Cadmium	8.00	78.7	54.1	13.1	7.61
Copper	177	524	218	1 530	97.3
Lead	2 310	8 410	7 880	5 180	4 610
Zinc	736	4 240	3 720	1 200	835
Weight of matter collected in 24 hr (mg)	2.70	0.69	0.94	1.61	2.61
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	0.6	0
Air temperature (5pm) (°C)	21	20	17	15	10
Mean wind speed (5pm–5pm) (Kts)	13	12	9	13	10
Mean wind direction (5pm–5pm)	NNW	NW	NW	NW	SSW

Month and year: November 1988	Dates samples taken				
	20–21	21–22	23–24	24-25	25-26
Concentration in air (ng m^{-3})					
Cadmium	0.160	0.145	0.339	0.117	0.073
Copper	1.84	5.12	6.11	1.78	1.05
Lead	72.6	36.9	48.6	48.8	70.2
Zinc	15.6	39.1	22.7	17.5	12.6
Concentration in particulates (µg g^{-1})					
Cadmium	22.0	10.5	27.5	8.29	3.97
Copper	252	372	496	126	56.9
Lead	9 960	2 680	3 940	3 460	3 820
Zinc	2 140	2 830	1 840	1 240	685
Weight of matter collected in 24 hr (mg)	0.93	1.50	1.36	1.55	2.06
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	0	0
Air temperature (5pm) (°C)	12	14	18	15	16
Mean wind speed (5pm–5pm) (Kts)	7	10	6	14	13
Mean wind direction (5pm–5pm)	SSW	ENE	S	ENE	ENE

Appendix 7·2 continued...

Month and year: December 1988	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.093	0.163	0.057	0.072	0.273
Copper	2.86	2.38	0.449	1.62	10.4
Lead	74.0	82.9	81.4	108	71.8
Zinc	38.4	11.0	8.11	26.2	30.7
Concentration in particulates (μg g^{-1})					
Cadmium	3.62	12.2	4.66	1.45	14.8
Copper	112	179	36.4	30.6	561
Lead	2 890	6 420	6 610	2 180	3 880
Zinc	1 500	829	658	530	1 660
Weight of matter collected in 24 hr (mg)	2.88	1.42	1.34	5.74	1.88
Climatological data					
Rainfall (5pm–5pm) (mm)	0	1.5	0	0	0
Air temperature (5pm) (°C)	21	27	14	18	18
Mean wind speed (5pm–5pm) (Kts)	8	13	10	15	17
Mean wind direction (5pm–5pm)	ENE	WNW	S	E	E

Month and year: January 1989	Dates samples taken				
	20–21	21–22	22–23	23-24	24-25
Concentration in air (ng m^{-3})					
Cadmium	0.102	0.294	0.065	0.043	0.396
Copper	6.66	6.37	3.42	4.12	7.33
Lead	48.0	81.4	35.6	41.2	49.5
Zinc	27.3	14.2	25.3	14.2	21.0
Concentration in particulates (μg g^{-1})					
Cadmium	7.12	16.1	2.16	4.42	25.7
Copper	463	348	113	426	476
Lead	3 340	4 450	1 180	4 260	3 220
Zinc	1 900	776	840	1 470	1 360
Weight of matter collected in 24 hr (mg)	1.56	1.99	3.53	1.10	1.62
Climatological data					
Rainfall (5pm–5pm) (mm)	0	0	0	4.6	0
Air temperature (5pm) (°C)	21	29	29	22	19
Mean wind speed (5pm–5pm) (Kts)	10	10	14	8	10
Mean wind direction (5pm–5pm)	E	NNW	NNW	S	ENE

Appendix 7·3 (section 7·3·1)

Procedure for identification of outlying observations in a data set of 20 (from Grubbs, 1969).

1. Rank the observations in order: $x_1, x_2, x_3, \ldots x_{20}$. ($x_{20}$ is the suspected outlier);
2. Calculate the mean value of all observations;
3. Calculate $T_n = (x_{20} - \text{mean})/\sigma_{n-1}$
4. If T_n exceeds 2.56 (for 20 observations), it would occur by chance with a probability of less than 5%.

Appendix 7·4 (section 7·3·1)

Summary statistics relating to site 1 for the months June 1987 to January 1988 (n = 40).

Variable	Arithmetic mean	Standard deviation	95% error on mean[a]	Geometric mean	Range Lowest	Range Highest
Concentration in air (ng m^{-3})						
Cadmium	0.494	0.304	±0.097	0.409	0.117	1.17
Copper	13.1	8.0	±2.6	11.2	2.88	42.0
Lead	160	142	±45	123	28.9	699
Zinc	46.3	36.9	±11.8	38.6	20	203
Concentration in particulates (μg g^{-1})						
Cadmium	27.9	27.0	±8.6	20.5	2.56	133
Copper	693	574	±184	541	100	3 260
Lead	6 810	3 590	±1 150	5 910	1 440	15 300
Zinc	2 510	3 340	±1 070	1 860	532	21 900
Weight collected in 24 hr	3.02	1.99	±0.64	2.48	0.490	9.40
Rainfall (mm) (5pm–5pm)	1.7	5.4	±2		0	30.9
Air temperature at 5pm (°C)	14	5	±2	13	7	24
Mean wind speed (5pm–5pm) (kts)	9	4	±1	8	1	19

Appendix 7·5 (section 7·3·2)

Monthly means, standard deviations, errors on means and medians of the various parameters measured in the survey of Christchurch airborne particulates.

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
ngCd m^{-3}					
	Site 1 (Avonside)				
	June 1987	0.729	0.326	±0.327	0.735
	July 1987	0.809	0.278	±0.296	0.826
	August 1987	0.487	0.269	±0.287	0.444
	September 1987	0.566	0.390	±0.416	0.450
	October 1987	0.366	0.161	±0.172	0.328
	November 1987	0.321	0.319	±0.340	0.152
	December 1987	0.297	0.093	±0.100	0.311
	January 1988	0.373	0.184	±0.196	0.343
	February 1988	0.370	0.153	±0.163	0.350
	March 1988	1.56	2.44	±2.60	0.675
	April 1988	2.15	2.52	±2.69	0.882
	May 1988	2.11	1.02	±1.09	1.68
	Site 2 (Huntsbury)				
	June 1988	0.939	0.519	±0.553	0.744
	July 1988	0.551	0.148	±0.157	0.636
	August 1988	0.749	0.643	±0.686	0.481
	September 1988	0.727	0.680	±0.725	0.563
	October 1988	0.302	0.159	±0.170	0.196
	November 1988	0.167	0.102	±0.109	0.145
	December 1988	0.132	0.088	±0.095	0.093
	January 1989	0.180	0.156	±0.167	0.102
ngCu m^{-3}					
	Site 1 (Avonside)				
	June 1987	20.0	14.7	±15.7	15.0
	July 1987	12.6	9.1	±9.7	11.0
	August 1987	8.77	2.27	±2.42	8.65
	September 1987	15.6	7.1	±7.6	14.9
	October 1987	6.82	3.80	±4.05	4.91
	November 1987	15.0	8.4	±8.9	10.4
	December 1987	12.3	3.4	±3.6	10.8
	January 1988	13.8	4.7	±5.0	12.8
	February 1988	9.03	3.54	±3.78	8.13
	March 1988	12.1	13.1	±14.0	7.72
	April 1988	26.4	13.8	±14.7	23.9
	May 1988	41.7	26.5	±28.2	35.7
	Site 2 (Huntsbury)				
	June 1988	146 (85.3)[b]	116	±124	136 (66.9)[b]
	July 1988	99.6 (69.3)[b]	98.1	±105	56.3 (41.9)[b]
	August 1988	47.0	69.3	±73.9	15.8
	September 1988	155 (9.60)[b]	325	±347	11.8 (10.1)[b]
	October 1988	6.72	8.59	±9.16	3.08
	November 1988	3.18	2.27	±2.42	1.84
	December 1988	3.54	3.94	±4.20	2.38
	January 1989	5.58	1.71	±1.82	6.37

Appendix 7·5 continued...

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
ngPb m^{-3}					
Site 1 (Avonside)					
	June 1987	342	265	±282	179
	July 1987	312	110	±117	317
	August 1987	120	77	±82	82.9
	September 1987	151	15	±16	156
	October 1987	109	78	±83	72.4
	November 1987	58.2	26.3	±28.0	53.0
	December 1987	101	32	±34	94.1
	January 1988	87.4	25.9	±27.6	81.8
	February 1988	107	52	±55	133
	March 1988	162	55	±59	161
	April 1988	425	211	±225	501
	May 1988	818	362	±386	872
Site 2 (Huntsbury)					
	June 1988	117	59	±63	139
	July 1988	70.5	23.2	±24.7	60.5
	August 1988	83.2	42.2	±45.0	83.7
	September 1988	88.5	42.5	±45.3	74.4
	October 1988	71.4	21.3	±22.8	71.1
	November 1988	55.4	15.4	±16.4	48.8
	December 1988	83.6	14.4	±15.4	81.4
	January 1989	51.1	17.9	±19.0	48.0
ngZn m^{-3}					
Site 1 (Avonside)					
	June 1987	79.6	71.9	±76.6	58.0
	July 1987	59.2	40.9	±43.6	51.0
	August 1987	31.4	5.7	±6.1	30.8
	September 1987	53.9	24.0	±25.6	46.2
	October 1987	34.5	10.8	±11.5	29.0
	November 1987	49.2	53.6	±57.1	24.5
	December 1987	33.0	9.0	±10.0	30.4
	January 1988	29.6	5.6	±6.0	31.9
	February 1988	22.5	9.3	±9.9	23.2
	March 1988	92.5	91.8	±97.9	41.8
	April 1988	253	367	±391	77.3
	May 1988	149	32	±34	138
Site 2 (Huntsbury)					
	June 1988	41.8	23.2	24.8	44.3
	July 1988	18.7	5.6	±6.0	16.0
	August 1988	31.5	21.6	±23.1	30.7
	September 1988	27.5	20.3	±21.6	20.3
	October 1988	22.6	6.9	±7.3	19.0
	November 1988	21.5	10.5	±11.2	17.5
	December 1988	22.9	13.0	±13.8	26.2
	January 1989	20.4	6.10	±6.5	21.0

Appendix 7·5 continued...

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
µgCd g^{-1}					
Site 1 (Avonside)					
	June 1987	23.2	7.4	±7.9	21.1
	July 1987	22.0	12.5	±13.3	19.0
	August 1987	36.9	19.3	±20.6	39.0
	September 1987	42.8	47.5	±50.6	29.9
	October 1987	23.6	12.3	±13.1	23.7
	November 1987	39.5	53.0	±56.5	14.2
	December 1987	15.7	6.1	±6.5	17.6
	January 1988	19.5	18.7	±19.9	11.1
	February 1988	23.7	16.4	±17.5	19.0
	March 1988	68.8	95.6	±102	41.7
	April 1988	44.5	42.4	±45.2	18.3
	May 1988	20.9	9.0	±9.6	20.4
Site 2 (Huntsbury)					
	June 1988	72.4	72.3	±77.1	56.5
	July 1988	39.5	11.1	±11.9	41.1
	August 1988	46.0	32.0	±34.1	30.9
	September 1988	49.5	24.2	±25.8	60.4
	October 1988	32.3	32.3	±34.4	13.1
	November 1988	14.5	9.9	±10.5	10.5
	December 1988	7.35	5.80	±6.19	4.66
	January 1989	11.1	9.73	±10.4	7.12
µgCu g^{-1}					
Site 1 (Avonside)					
	June 1987	687	402	±429	757
	July 1987	369	234	±249	296
	August 1987	721	423	±451	662
	September 1987	478	177	±189	378
	October 1987	449	323	±344	346
	November 1987	1 560	1 150	±1 230	1 320
	December 1987	662	302	±322	693
	January 1988	614	180	±192	550
	February 1988	601	408	±435	385
	March 1988	555	524	±559	504
	April 1988	471	201	±214	384
	May 1988	329	73	±78	330
Site 2 (Huntsbury)					
	June 1988	12 000 (3 730)[b]	17 200	±18 300	6 000 (3 100)[b]
	July 1988	7 330 (3 940)[b]	8 520	±9 080	3 550 (2 260)[b]
	August 1988	3 110	3 750	±4 000	991
	September 1988	35 500 (589)[b]	78 000	± 83 100	561 (438)[b]
	October 1988	509	593	±632	218
	November 1988	261	179	±190	252
	December 1988	184	219	±234	112
	January 1989	365	150	±159	426

Appendix 7·5 continued...

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
µgPb g^{-1}					
Site 1 (Avonside)					
	June 1987	9 510	4 110	±4 380	7 840
	July 1987	9 180	2 950	±3 140	9 890
	August 1987	8 390	4 510	±4 810	6 330
	September 1987	5 120	1 830	±1 950	5 190
	October 1987	6 160	2 320	±2 470	5 500
	November 1987	6 790	5 350	±5 700	5 180
	December 1987	5 230	1 840	±1 960	4 720
	January 1988	4 070	1 820	±1 940	4 150
	February 1988	6 000	2 460	±2 620	4 890
	March 1988	7 540	3 330	±3 550	6 990
	April 1988	9 800	2 790	±2 790	10 400
	May 1988	7 860	2 610	±2 780	8 530
Site 2 (Huntsbury)					
	June 1988	6 210	2 850	±3 040	5 820
	July 1988	5 350	2 650	±2 820	3 820
	August 1988	6 710	3 850	±4 100	5 260
	September 1988	7 960	6 090	±6 490	6 010
	October 1988	5 680	2 500	±2 670	5 180
	November 1988	4 770	2 940	±3 140	3 820
	December 1988	4 360	1 980	±2 110	3 880
	January 1989	3 290	1 300	±1 380	3 340
µgZn g^{-1}					
Site 1 (Avonside)					
	June 1987	2 070	690	±740	1 660
	July 1987	1 720	1 140	±1 220	1 200
	August 1987	2 640	1 760	±1 880	2 350
	September 1987	1 890	1 250	±1 330	1 670
	October 1987	2 330	1 200	±1 280	2 600
	November 1987	6 300	8 840	±9 420	1 990
	December 1987	1 690	500	±540	1 910
	January 1988	1 450	810	±890	1 160
	February 1988	1 380	840	±900	1 090
	March 1988	4 050	3 550	±3 780	3 060
	April 1988	6 060	6 150	±6 560	2 380
	May 1988	1 510	340	±360	1 540
Site 2 (Huntsbury)					
	June 1988	2 570	2 030	±2 170	1 870
	July 1988	1 360	520	±550	1 360
	August 1988	2 040	1 130	±1 210	1 840
	September 1988	2 480	2 310	±2 460	1 750
	October 1988	2 150	1 690	±1 800	1 200
	November 1988	1 750	830	±880	1 840
	December 1988	1 040	510	±550	829
	January 1989	1 270	470	±500	1 360

Appendix 7·5 continued...

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
Weight collected in 24 hr (mg)					
Site 1 (Avonside)					
	June 1987	4.20	2.80	±2.98	3.97
	July 1987	4.07	1.28	±1.36	4.30
	August 1987	1.87	1.17	±1.25	1.48
	September 1987	3.98	2.15	±2.29	3.26
	October 1987	3.67	3.27	±3.49	2.44
	November 1987	1.40	0.72	±0.77	1.71
	December 1987	2.32	0.81	±0.86	2.52
	January 1988	2.65	0.93	±0.99	3.06
	February 1988	2.18	1.12	±1.19	1.91
	March 1988	2.65	0.99	±1.06	2.58
	April 1988	4.61	1.70	±1.81	4.90
	May 1988	10.8	2.0	±2.1	10.4
Site 2 (Huntsbury)					
	June 1988	2.94	2.23	±2.38	2.82
	July 1988	2.07	1.18	±1.26	1.98
	August 1988	1.97	1.05	±1.12	2.07
	September 1988	1.75	0.38	±0.41	1.56
	October 1988	1.71	0.93	±0.99	1.61
	November 1988	1.48	0.41	±0.43	1.50
	December 1988	2.65	1.83	±1.95	1.88
	January 1989	1.96	0.93	±0.99	1.62
Rainfall (mm) (5pm–5pm)					
Site 1 (Avonside)					
	June 1987	9.1	13.6	±14.5	0.4
	July 1987	1.2	1.7	±1.8	0.5
	August 1987	0.1	0.1	±1.3	0.1
	September 1987	0.2	0.2	±0.2	0
	October 1987	0	0	0	0
	November 1987	0.1	0.2	±0.2	0
	December 1987	1.8	2.6	±2.8	0
	January 1988	0.2	0.5	±0.6	0
	February 1988	3.9	4.7	±5.0	1.9
	March 1988	0.2	0.5	±0.5	0
	April 1988	0	0	0	0
	May 1988	1.2	2.7	±2.9	0
Site 2 (Huntsbury)					
	June 1988	0.3	0.4	±0.4	0
	July 1988	0.7	1.5	±1.6	0
	August 1988	1.5	2.1	±2.3	0
	September 1988	0.6	1.3	±1.4	0
	October 1988	0.1	0.3	±0.3	0
	November 1988	0	0	0	0
	December 1988	0.3	0.7	±0.7	0
	January 1989	0.9	2.1	±2.2	0

Appendix 7·5 continued...

Parameter	Year & month	Mean	Standard deviation	95% error on mean[a]	Median
Air temperature at 5pm (°C)					
Site 1 (Avonside)					
	June 1987	7	0	0	7
	July 1987	7	0	0	7
	August 1987	10	2	±2	10
	September 1987	11	1	±1	12
	October 1987	17	3	±3	17
	November 1987	17	1	±1	17
	December 1987	19	4	±4	21
	January 1988	20	3	±3	20
	February 1988	21	4	±4	22
	March 1988	14	2	±2	14
	April 1988	11	1	±1	11
	May 1988	6	2	±3	6
Site 2 (Huntsbury)					
	June 1988	7	2	±2	7
	July 1988	10	4	±4	8
	August 1988	9	3	±3	9
	September 1988	15	4	±4	14
	October 1988	17	4	±5	17
	November 1988	15	2	±2	15
	December 1988	20	5	±5	18
	January 1989	24	5	±5	22
Mean wind speed (5pm–5pm)					
Site 1 (Avonside)					
	June 1987	5	3	±3	3
	July 1987	5	4	±4	3
	August 1987	9	3	±3	9
	September 1987	10	4	±4	9
	October 1987	9	3	±3	9
	November 1987	11	1	±1	12
	December 1987	12	4	±4	11
	January 1988	8	2	±2	8
	February 1988	11	3	±3	12
	March 1988	7	1	±2	7
	April 1988	5	1	±1	5
	May 1988	4	1	±1	4
Site 2 (Huntsbury)					
	June 1988	4	2	±2	4
	July 1988	7	4	±4	6
	August 1988	8	4	±4	8
	September 1988	6	2	±2	6
	October 1988	11	2	±2	12
	November 1988	10	4	±4	10
	December 1988	13	4	±4	13
	January 1989	10	2	±2	10

Notes: **a.** Student's t-test error on mean.
b. With outliers removed.

Appendix 7·6 (section 7·3·3a)

Correlation matrix between all variables relating to samples collected at site 1 except "wind direction". Number of pairs = 60. Probabilities[a] are as follows:
R>0.411, p<0.001; R>0.328, p<0.01; R>0.298, p<0.02; R>0.252, p<0.05.

	Natural logarithm of concentration in air (ng m^{-3}) of...				Natural logarithm of concentration in particulates (µg g^{-1}) of...			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Natural log of...								
ngCd m^{-3}	1							
ngCu m^{-3}	0.563	1						
ngPb m^{-3}	0.705	0.424	1					
ngZn m^{-3}	0.801	0.628	0.710	1				
µgCd g^{-1}	0.588	0.234	0.066	0.408	1			
µgCu g^{-1}	0.021	0.403	–0.406	0.006	0.556	1		
µgPb g^{-1}	0.431	0.030	0.538	0.356	0.533	0.111	1	
µgZn g^{-1}	0.393	0.233	0.004	0.554	0.780	0.576	0.484	1
Weight (mg)	0.502	0.353	0.738	0.555	–0.256	–0.594	–0.057	–0.289
Rainfall (mm)	–0.050	–0.030	–0.128	–0.130	0.146	0.244	0.124	0.090
Air temp (°C)	–0.461	–0.298	–0.596	–0.465	–0.137	0.165	–0.401	–0.105
Wind spd (Kts)	–0.567	–0.255	–0.637	–0.489	–0.173	0.327	–0.339	–0.045

	ln[Weight (mg)]	Rainfall (mm)	Air temp (°C)	Wind spd (Kts)
Rainfall (mm)	–0.254	1		
Air temp (°C)	–0.388	–0.126	1	
Wind spd (Kts)	–0.545	0.131	0.505	1

Note: a. According to Pearson's Tables.

Appendix 7·7 (section 7·3·3a)

Correlation matrix between all variables relating to samples collected at site 2 except "wind direction". Number of pairs = 36. Probabilities[a] are as follows:
R>0.526, p<0.001; R>0.424, p<0.01; R>0.387, p<0.02; R>0.330, p<0.05.

	Natural logarithm of concentration in air (ng m^{-3}) of...				Natural logarithm of concentration in particulates (µg g^{-1}) of...			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Natural log of...								
ngCd m^{-3}	1							
ngCu m^{-3}	0.687	1						
ngPb m^{-3}	0.428	0.227	1					
ngZn m^{-3}	0.531	0.461	0.449	1				
µgCd g^{-1}	0.822	0.539	0.018	0.202	1			
µgCu g^{-1}	0.647	0.931	–0.005	0.280	0.686	1		
µgPb g^{-1}	0.363	0.129	0.142	–0.054	0.685	0.320	1	
µgZn g^{-1}	0.362	0.260	–0.264	0.379	0.687	0.449	0.626	1

Appendix 7·7 continued...

	Natural logarithm of concentration in air (ng m^{-3}) of...				Natural logarithm of concentration in particulates (μg g^{-1}) of...			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
ln[Weight (mg)]	0.076	0.228	0.618	0.428	–0.460	–0.124	–0.556	–0.594
Rainfall (mm)	–0.125	0.056	–0.351	–0.382	0.058	0.225	0.026	–0.020
Air temp (°C)	–0.495	–0.471	–0.236	–0.172	–0.472	–0.506	–0.304	–0.220
Wind spd (Kts)	–0.628	–0.557	–0.448	–0.442	–0.484	–0.481	–0.295	–0.262

	ln[Weight (mg)]	Rainfall (mm)	Air temp (°C)	Wind spd (Kts)
Rainfall (mm)	–0.230	1		
Air temp (°C)	0.021	–0.144	1	
Wind spd (Kts)	–0.201	0.054	0.469	1

Note: a. According to Pearson's Tables.

Appendix 7·8 (section 7·3·3a)

The most significant correlations present between concentrations of cadmium, copper, lead, zinc, the weight of material collected in 24 hr (mg) and meteorological parameters relating to site 2, and their degrees of significance. Least-squares equations are given in cases where the correlation is highly significant. (Number of data pairs = 36).

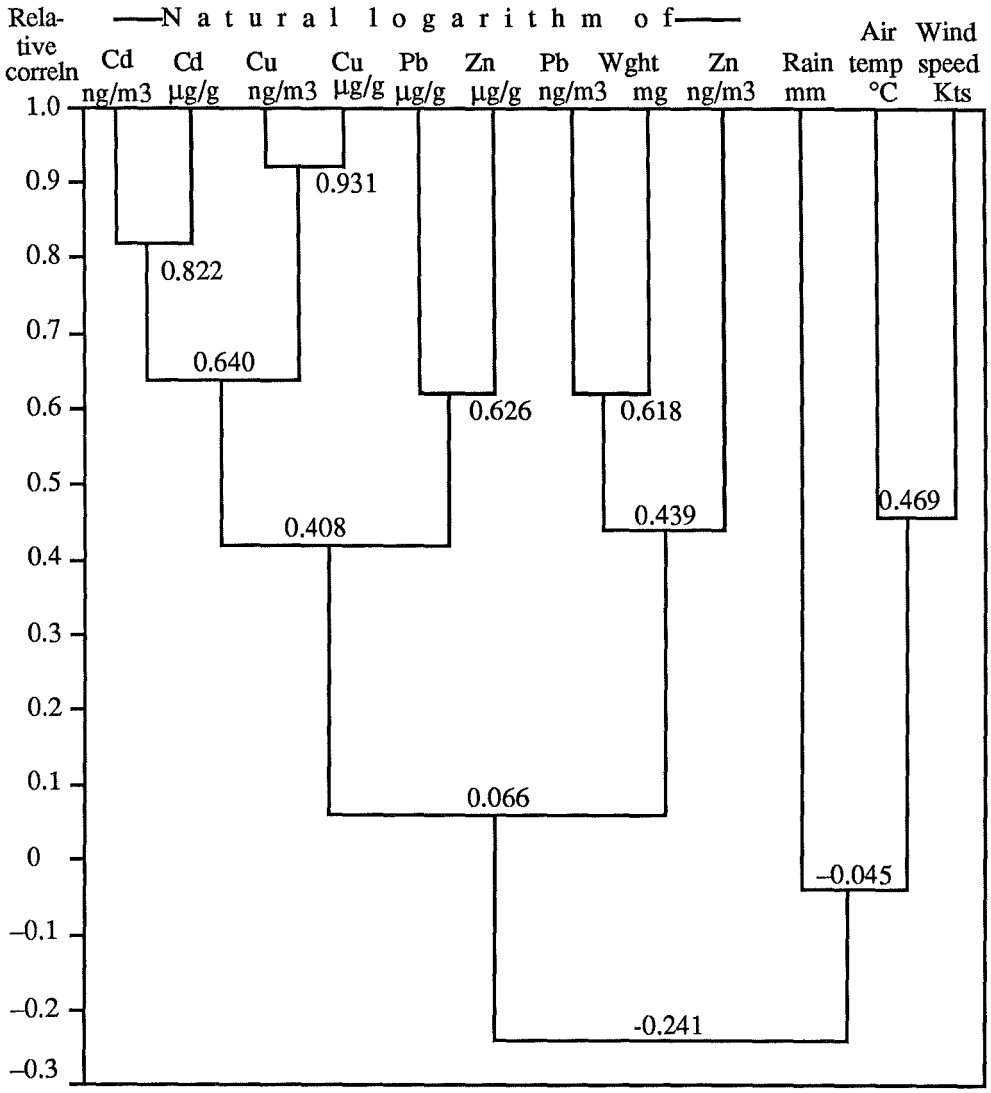
Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[ngCd m^{-3}] with...				
ln[ngCu m^{-3}]	0.687	<0.001	Highly	ln[ngCd m^{-3}] = 0.47ln[ngCu m^{-3}]–2.24
ln[ngPb m^{-3}]	0.428	<0.01	Very	
ln[ngZn m^{-3}]	0.531	<0.001	Highly	ln[ngCd m^{-3}] = 1.25ln[ngZn m^{-3}]–9.21
ln[μgCd g^{-1}]	0.822	<0.001	Highly	ln[ngCd m^{-3}] = 0.72ln[μgCd g^{-1}]–3.35
ln[μgCu g^{-1}]	0.647	<0.001	Highly	ln[ngCd m^{-3}] = 0.45ln[μgCu g^{-1}]–4.05
ln[μgPb g^{-1}]	0.363	<0.05	Just	
ln[μgZn g^{-1}]	0.362	<0.05	Just	
Air temperature (°C)	–0.495	<0.05	Very	
Mean wind speed (Kts)	–0.628	<0.001	Highly	ln[ngCd m^{-3}] = 0.21–0.16[Wind spd (Kts)]
ln[ngCu m^{-3}] with...				
ln[ngZn m^{-3}]	0.461	<0.02	Quite	
ln[μgCd g^{-1}]	0.539	<0.001	Highly	ln[ngCu m^{-3}] = 0.73ln[μgCd g^{-1}]
ln[μgCu g^{-1}]	0.931	<0.001	Highly	ln[ngCu m^{-3}] = 0.93ln[μgCu g^{-1}]–3.74
Air temperature (°C)	–0.471	<0.01	Very	
Mean wind speed (Kts)	–0.557	<0.001	Highly	ln[ngCd m^{-3}] = 4.08–0.22[Wind spd (Kts)]
ln[ngPb m^{-3}] with...				
ln[ngZn m^{-3}]	0.449	<0.01	Very	
ln[Weight (mg)]	0.618	<0.001	Highly	ln[ngPb m^{-3}] = 0.47ln[mg]+3.99
Rainfall (mm)	–0.351	<0.05	Just	
Mean wind speed (Kts)	–0.448	<0.001	Very	

Appendix 7·8 continued...

Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[ngZn m^{-3}] with...				
ln[µgZn g^{-1}]	0.379	<0.05	Just	
ln[Weight (mg)]	0.428	<0.01	Very	
Rainfall (mm)	–0.382	<0.05	Just	
Mean wind speed (Kts)	–0.442	<0.01	Very	
ln[µgCd g^{-1}] with...				
ln[µgCu g^{-1}]	0.686	<0.001	Highly	ln[µgCd g^{-1}] = 0.51ln[µgCu g^{-1}]–0.30
ln[µgPb g^{-1}]	0.685	<0.001	Highly	ln[µgCd g^{-1}] = 1.44ln[µgPb g^{-1}]–9.21
ln[µgZn g^{-1}]	0.687	<0.001	Highly	ln[µgCd g^{-1}] = 1.25ln[µgZn g^{-1}]-6.14
ln[Weight (mg)]	–0.460	<0.01	Very	
Air temperature (°C)	–0.472	<0.01	Very	
Mean wind speed (Kts)	–0.484	<0.01	Very	
ln[µgCu g^{-1}] with...				
ln[µgZn g^{-1}]	0.449	<0.01	Very	
Air temperature (°C)	–0.506	<0.01	Very	
Mean wind speed (Kts)	–0.481	<0.01	Very	
ln[µgPb g^{-1}] with...				
ln[µgZn g^{-1}]	0.626	<0.001	Highly	ln[µgPb g^{-1}] = 0.54ln[µgZn g^{-1}]+4.52
ln[Weight (mg)]	–0.526	<0.001	Highly	ln[ngPb m^{-3}] = 8.75–0.48ln[mg]
ln[µgZn g^{-1}] with...				
ln[Weight (mg)]	–0.594	<0.001	Highly	ln[µgZn g^{-1}] = 7.64–0.59ln[mg]
Air temp (°C) with...				
Mean wind speed (Kts)	0.469	<0.01	Very	

Appendix 7·9 (section 7·3·3a)

Dendogram showing relative interrelationships between variables in the site 2 (Huntsbury) data set.



Appendix 7·10 (section 7·3·3b)

Factor score weights of the oblique transformation solution (Orthotran/Varimax) of the Principal Components Analysis of the site 2 airborne particulates data.

Variable	Factor 1	Factor 2	Factor 3
ngCd m^{-3}	0.222	0.090	0.026
ngPb m^{-3}	0.283	–0.121	0.056
ngZn m^{-3}	0.170	0.083	0.300
µgCd g^{-1}	0.064	0.257	–0.062
µgPb g^{-1}	–0.021	0.283	–0.012
µgZn g^{-1}	–0.092	0.355	0.175
Wght/24 hr (mg)	0.217	–0.284	0.106
Rainfall (mm)	0.019	–0.037	–0.593
Air temp (°C)	–0.234	0.057	0.467
Mn wind spd (Kts)	–0.265	0.051	0.203
Proportionate variance contributions (%)	43.4	38.0	18.6

CHAPTER 8
SEASONAL VARIATIONS IN THE CONCENTRATIONS OF CADMIUM, COPPER, LEAD AND ZINC IN CHRISTCHURCH TREE LEAVES

8·1 Introduction

Trace metals associated with leaves originate from two sources: the growth medium of the plant and the atmosphere. Uptake of metals by plant roots from the growth medium can be an active (metabolic) or passive (nonmetabolic) process (Hewitt and Smith, 1975; Kabata-Pendias and Pendias, 1984; Mengel and Kirkby, 1979; Robb and Pierpont, 1983). Metals directly deposited on a leaf can either remain on the leaf surface, or be (actively or passively) translocated into the leaf (Kabata-Pendias and Pendias, 1984).

Several factors have been found to influence the rate at which cadmium is taken up by plant roots. These include genetic factors (cadmium uptake varies from species to species), the amount of cadmium already taken up, the transpiration rate, soil pH, soil cation exchange capacity, soil cation content, soil organic content, soil phosphorus content and soil cadmium content (Haghiri, 1976; Jastrow and Koeppe, 1980; Lepp, 1981; Symeonides and McRae, 1977).

In terms of the four metals examined in this survey, cadmium and lead are non-essential and toxic to plants, whereas copper and zinc are regarded as being essential for plant growth (Hewitt and Smith, 1975; Lepp, 1981; Mengel and Kirkby, 1979). Most of the copper in plants is complexed with low molecular weight organic compounds and with various proteins, and most of the zinc is associated with enzymes (Baker and Hall, 1988; Kabata-Pendias and Pendias, 1984). Both copper and zinc are utilized by plants in protein and carbohydrate metabolism; copper itself is also associated with photosynthesis and oxidation processes.

Seasonal variations in trace element concentrations in plants can in some cases be accounted for by seasonal changes in plant morphology. Crump *et al.* (1980) studied seasonal variations in the lead levels of a pasture grass growing near a motorway, and found that there was a large reduction in the concentration of lead in the grass during spring. This was thought to be due to the rapid spring growth of the grass causing dilution.

The main purpose of this study was to monitor (and attempt to explain) temporal variations in the concentrations of cadmium in the leaves of a deciduous tree. The advantage of sampling from a deciduous tree is that leaves collected at the beginning of the growing season represent a minimum in terms of trace metal deposition from the atmosphere. Concentrations of copper, lead and zinc in tree leaves were also measured because of cadmium's geochemical association with these metals (section 1·3·1).

8·2 Method

8·2·1 Selection, collection and handling of samples

Horse chestnut (*Aesculus hippocastanum L.*) trees were chosen for this study for two reasons. Firstly, the horse chestnut is a deciduous tree. Secondly, the choice of sampling sites was not limited by the distribution of horse chestnut trees, as they are found in most areas of Christchurch.

Trees were sampled at each of six parks, the positions of which are shown in Appendix 3·1 (inside back cover). One of these parks (Latimer Square) is in the central city. The other five (Mahars Road Playground, Avon Park, Erie Monro Playground, Barrington Park and University Drive) are in suburban areas and are approximately N, NE, SE, SW and NW of the central city (respectively). Throughout this Chapter, the sampling sites will be referred to as follows: Avon Park, site 1; Barrington Park, site 2; Erie Monro Playground, site 3; Latimer Square, site 4; Mahars Road Playground, site 5; University Drive, site 6. In terms of traffic density, sites 2–4 (Latimer Square, Erie Monro Playground and Barrington Park) were situated near (less than 5 m from) main roads, whereas sites 1, 5 and 6 (Mahars Road Playground, Avon Park and University Drive) were next to "moderately" used roads.

Leaf samples were collected from a single tree at each location at monthly intervals for seven consecutive months. Sampling commenced in October 1987 (mid spring) and finished in April 1988 (mid-autumn), when the trees lost their leaves. The actual sampling dates were 9 October 1987, 10 November 1987, 8 December 1987, 8 January 1988, 8 February 1988, 10 March 1988 and 6 April 1988. Leaves on the trees at sampling sites 2 and 4 were shed early, and were not sampled in April 1988.

Samples were collected from the lower regions of each tree at a height of 4–5 m. Plastic disposable gloves were used when handling the leaves, which were stored in clean plastic bags. Three leaves were gathered from each of four equally spaced locations around each tree (the first of these locations was the "side" nearest the road and the others were taken as being relative to that).

The total surface area (cm^2) of each sample of 12 leaves was estimated by spreading all the leaves in the sample over clean plastic sheets in an area-filling manner. The aggregate surface area of the 12 leaves was taken as being equal to twice the area of plastic they covered. Each sample (12 leaves) was then dried at 60 °C for 72 hr and weighed, after which the quantity {dry weight : surface area} of the leaves in that sample was calculated (expressed in g cm^{-2}). Dried samples were crushed (in their bags) and homogenized.

A stainless-steel core extractor (of diameter 2.5 cm) was used to collect a soil core from each site on 9 May 1989. Cores were taken 2 m from the trunk of each tree (and at the same distance as the trunk of the tree from the roadside) and stored in clean plastic bags. They were then oven dried (105 °C) to constant weight, crushed, sieved (with particles coarser than 563 μm being discarded) and homogenized.

An attempt was made to indirectly assess the extent to which (wet or dry) deposition of material from the atmosphere influences trace metal levels in leaves. A method which has previously been used to gauge this parameter is the comparison of metal concentrations in washed leaves with those in unwashed leaves. This method has been found to be rather unreliable. For instance, washing can remove anything from 10 to 95% of surface lead from leaves (Fergusson *et al.* 1980). Additionally, washing does not remove atmospherically-derived metals which have since been incorporated into the leaf structure (section 8·1).

The method of measuring the effects of atmospheric deposition which was attempted in this study was as follows. Six holes were cut in one side of each of four large plastic bags. Waterproof tape was used to secure a membrane-filter (Millipore 48 mm diameter, pore-size 0.45 μm) over each hole. Each bag was placed, membrane-filter side down, over the branch of a different deciduous tree (apple, apricot, oak, pear) in early spring (September) 1988. At that time the trees involved were in bud. Bags were fastened securely to the trees, and the seal was made as air-tight as possible with waterproof tape. It was intended that, during photosynthesis and transpiration, the membrane-filters would mediate the entry of carbon dioxide to, and the exit of oxygen and water vapour from, the plastic bag. Comparison after a suitable time period of the metal concentrations of the leaves grown within the bag with those of the other leaves on the same tree would give a measure of the amount of atmospherically-derived metal.

Unfortunately, after three months, large quantities of water had condensed inside each bag, some leaves had started to rot, and the experiment was abandoned. (Among other things, the high humidity within the bags would have reduced the bagged leaves' transpiration rates, causing less water to be drawn to them from the roots; the contribution made by soil trace metals to the levels in the leaves would thus diminish (Kabata-Pendias and Pendias, 1985).) Photographs showing a bag on one of the trees at the beginning of the experiment and after three months are given in Appendix 8·1.

8·2·2 Digestion and analysis

Soil samples were digested and analysed using the method given in section 3·3·2.

Two portions of each sample of dried leaves (each weighing about 10 g) were placed in two 100 ml beakers and ashed overnight in a muffle furnace at 400 °C. The ash was boiled in 15 ml of 4 M nitric acid for 30 minutes. After cooling the solution was filtered (through an acid and double-distilled water washed Whatman No. 540 filter paper). The residue was washed with double-distilled water until the filtrate reached a volume of 25 ml.

Copper, lead and zinc concentrations in the digestion extracts were determined by FAAS, using the parameters given in Chapter 14. Background correction was used in all cases. Solutions were analysed for cadmium by GFAAS (with background correction) using the furnace heating program given in Table 8·1 (following page). Other parameters relating to the GFAAS determination of cadmium are given in Chapter 14. Using the furnace heating program given in Table 8·1, absorption peaks for cadmium were sharp, symmetrical, and in most cases above 0.050 in value.

Table 8·1

GFAAS furnace heating program for the measurement of cadmium in horse chestnut leaf extracts.

Step number	Step	Temperature (°C)	Ramp time (s)	Holding time (s)
1	Drying # 1	80	3	1
2	Drying # 2	120	2	2
3	Ashing	350	2	10
4	Atomization	2 000	2	1

The method of standard additions revealed that no significant interferences were present in the analyses of cadmium, copper, lead or zinc.

Five samples of certified-reference hay (V-10, International Atomic Energy Agency, Vienna) were analysed by this method for cadmium, lead and zinc. The results of the replicate analyses of certified-reference hay are given in Table 8·2.

Table 8·2

Given and measured concentrations of cadmium, copper, lead and zinc in certified-reference hay.

	Cadmium	Copper[a]	Lead	Zinc
Certified values				
Concentration ($\mu g\ g^{-1}$)	0.03	9.4	1.60	24
95% confidence interval	0.02–0.05	8.8–9.7	0.8–1.9	21–27
This study				
Number of analyses (n)	5	6	5	5
Mean concentration ($\mu g\ g^{-1}$)	0.027	8.15	1.55	21.2
Standard deviation ($\mu g\ g^{-1}$)	0.003	0.36	0.15	0.77
95% confidence interval[b]	0.024–0.030	7.83–8.47	1.40–1.70	20.4–22.0
Recovery[c] (%)	90	87	97	88

Notes: **a.** Copper data from Table 6·2.
b. Student's t-test error on mean.
c. Taken here as 100[mean value obtained in this study/certified value].

The recoveries and analytical precision in the analyses of cadmium, copper, lead and zinc in certified reference hay (Table 8·2) were considered to be satisfactory.

8·3 Results and discussion

8·3·1 Summary statistics

The ash weight concentrations of cadmium, copper, lead and zinc in all samples of horse chestnut leaves are given in Appendix 8·2. Values of the dry weight per unit area (g cm^{-2} x 10^5) of each sample of 12 leaves are presented in Appendix 8·3. Mean values (and 95% confidence errors) for the data at each site are given in Appendix 8·4. Statistics summarizing the data sets in Appendices 8·2 and 8·3 are listed in Table 8·3.

Table 8·3

Summary statistics of the ash weight concentrations of cadmium, copper, lead and zinc and the weight of leaves per unit area.

	Dry wt of leaves per unit surface area (g cm^{-2} x 10^5)	Cadmium (μg g^{-1})	Copper (μg g^{-1})	Lead (μg g^{-1})	Zinc (μg g^{-1})
Arithmetic mean	284	0.197	129	294	299
Std deviation	68	0.106	71	212	121
95% error[a]	±21	±0.034	±23	±63	±39
Geometric mean	276	0.177	110	228	280
Minimum	179	0.085	27.9	31.5	155
Maximum	442	0.489	333	1 100	708

Note: **a.** Student's t-test error on mean.

The means of the coefficients of variation of the ash weight concentrations of cadmium, copper, lead and zinc are 6%, 6%, 5% and 5%, respectively. These figures represent a relatively low degree of analytical scatter.

All of the data sets are positively skewed. It can be seen from the data in Table 8·3 that the geometric mean (ash weight) cadmium concentration in the horse chestnut leaves studied is 0.177 μg g^{-1}. Ash weight cadmium concentrations range from 0.085 μg g^{-1} (in leaves from site 6) to 0.489 μg g^{-1} (in leaves from site 2) (Table 8·3 and Appendix 8·2).

Interestingly, site 1, which is located near a moderately used road, has a slightly higher mean lead concentration than site 2 (located near a main road). Despite this, a single-tailed t-test (by computer) showed that overall, the highest concentrations of cadmium, copper and lead were found in leaves from trees at the three sites near main roads (sites 2,3 and 4). These three sites have a mean value of 1.7 times more cadmium (probability 99.94%), 1.5 times more copper (probability 99.5%) and 2.5 times more lead (probability 99.99%), than the three sites situated near moderately used roads. (Mean values and confidence intervals of the four metals and the figure [g cm^{-2} x 10^5] over sites 2–4 and those over sites 1, 5 and 6 are listed in Appendix 8·5.)

Concentrations of cadmium, copper, lead and zinc in the (0–8 cm) soil samples collected from the six sites are listed in Table 8·4. The relative ranking of the sites in terms of cadmium, copper, lead and zinc concentrations in soil (highest to lowest) are listed alongside relative rankings in terms of each metal's concentration in horse chestnut leaves in Table 8·5.

Table 8·4

Concentrations ($\mu g\ g^{-1}$) of cadmium, copper, lead and zinc in soil (0–8 cm) from the six sites.

Site number	Concentration ($\mu g\ g^{-1}$)			
	Cadmium	Copper	Lead	Zinc
1	0.089	8.86	29.9	50.8
2	0.153	15.8	72.0	88.9
3	0.230	17.7	218	101
4	0.313	60.4	216	141
5	0.390	17.7	154	183
6	0.115	8.39	76.3	79.6

Table 8·5

Rankings of the sites (highest to lowest) in terms of the concentrations of the four metals in soil and leaves.

Metal	Site numbers					
	Highest concn					Lowest concn
Cadmium						
Soil	5	4	3	2	6	1
Leaves	2	3	1	4	5	6
Copper						
Soil	4	3 = 5		2	1	6
Leaves	6	1	3	2	4	5
Lead						
Soil	3	4	5	6	2	1
Leaves	4	3	1	2	5 = 6	
Zinc						
Soil	5	4	3	2	6	1
Leaves	4	5	2	6	3	1

The following observations can be made from the data in Tables 8·4 and 8·5:

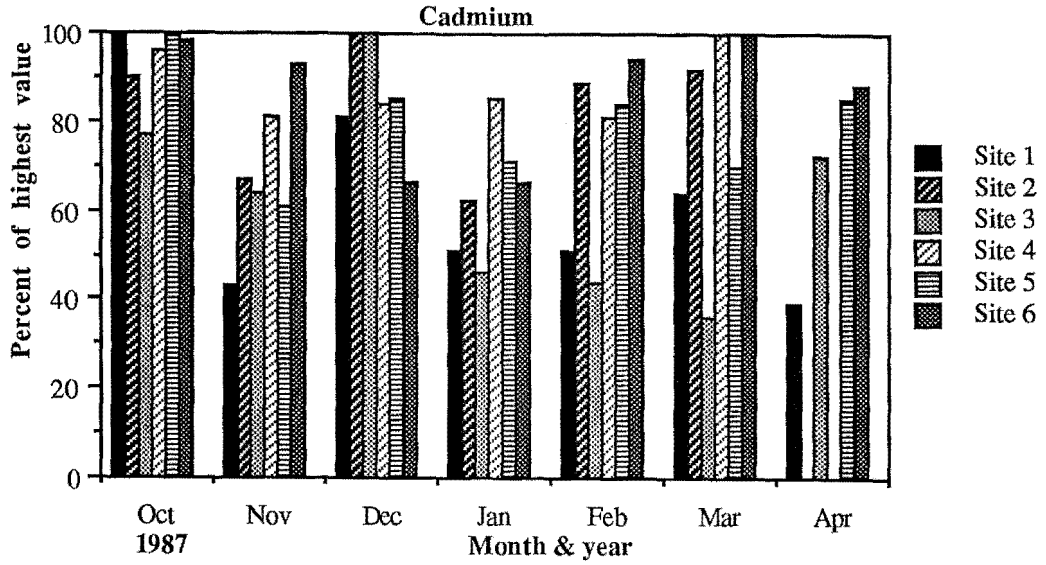
1. Soil concentrations of all four metals are in all cases highest at sites 3, 4 and 5.
2. The ranking in terms of cadmium concentrations in soils is identical to that of zinc. However, the rankings in terms of the concentrations of cadmium and zinc in leaves differ markedly from those of soils. This disparity could reflect different modes of entry of cadmium and zinc to the tree. For example, zinc uptake may be an active (metabolic) process whereas cadmium uptake may be a passive one (section 8·1). However, if cadmium uptake is limited by diffusion, and if most of the cadmium in the leaves is soil-derived, it would be expected that the highest leaf concentrations of cadmium would be found at those sites characterized by the highest cadmium soil concentrations. A more likely explanation for the disagreement is that a greater fraction of the cadmium on/in the leaves may be deposited from the atmosphere than is the case for zinc.
3. Concentrations of lead in both soil and leaves are highest at sites 3 and 4 (both of which are next to main roads). The high concentrations of lead in the leaves at these two sites could be a result both of more traffic-derived lead being directly deposited on the leaves, and of traffic-derived lead being deposited on the soil and subsequently leaching to (and being drawn up by) the roots. However, previous researchers have found that translocation of lead from the roots to the shoots of plants is minimal (about 3%) (Kabata-Pendias and Pendias, 1985). It would therefore appear reasonable to assume that most of the lead associated with the horse chestnut leaves at sites 3 and 4 was directly deposited from the atmosphere. Concentrations of lead in the soil at site 2, the other site situated near a main road, are comparatively low (Table 8·4). The probable reason for this is that at that site a (1.5 m) hedge is situated between the soil sampling site and the road.

8·3·2 Correlations and monthly variations

Figure 8·1 shows monthly variations in the ash weight concentrations of cadmium, copper, lead, zinc and the dry weight of leaves per unit area at each site, and is derived from the data in Appendix 8·2. Variables were transformed to their natural logarithms prior to the derivation of the correlation matrix, which is given in Appendix 8·6. A list of significant correlations and their least-squares equations is given in Table 8·6.

Figure 8·1

Monthly variations in the concentrations of cadmium, copper, lead and zinc in leaves from the six sites. Quantities are graphed as a percentage of the highest value.



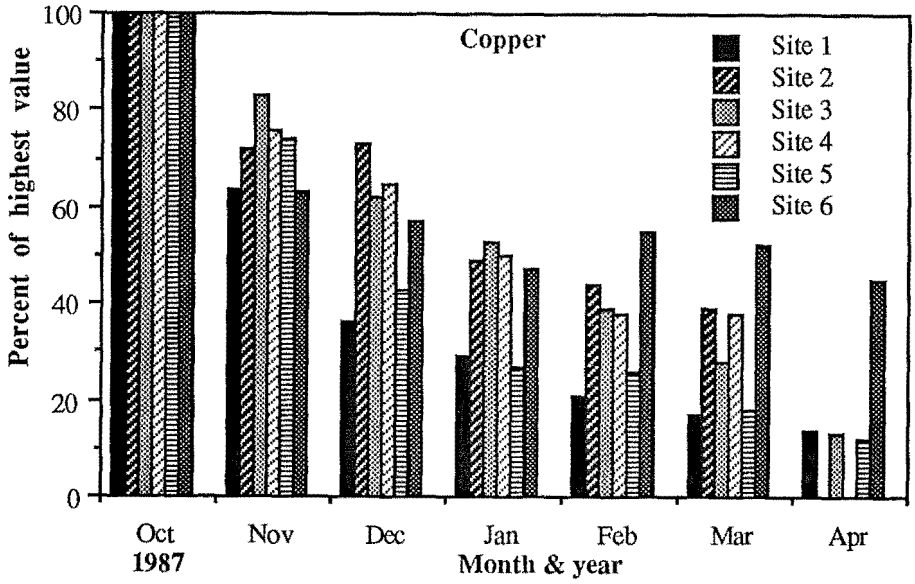
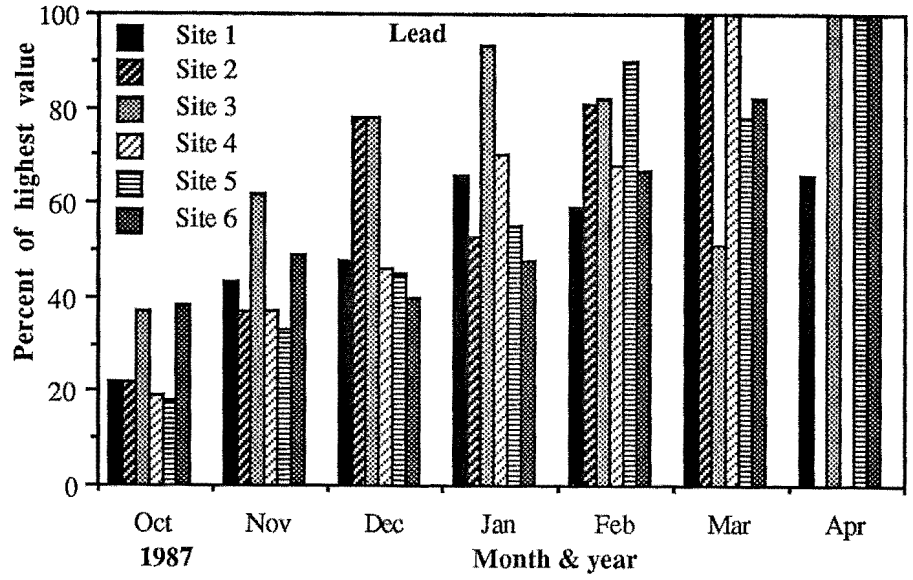


Figure 8·1 continued...



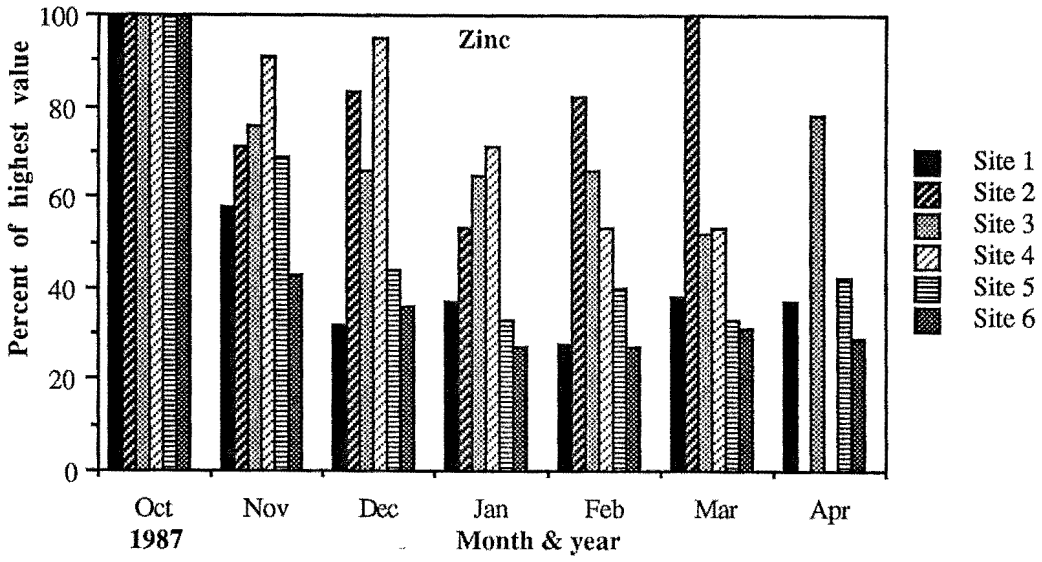


Figure 8·1 continued...

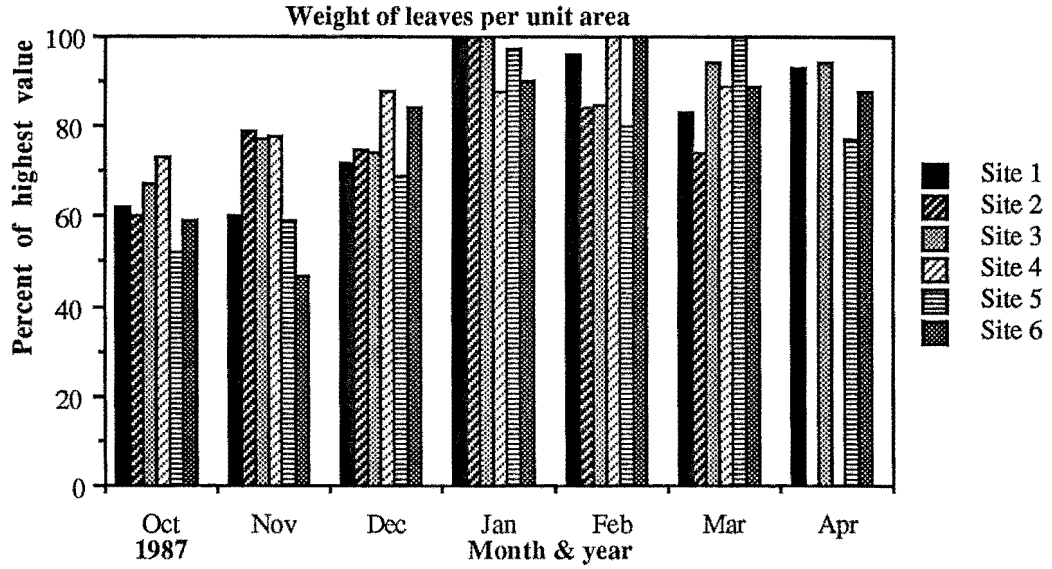


Table 8·6

Significant correlations between variables in the survey of horse chestnut leaves. Least-squares equations are given in for highly significant correlations. (Number of pairs = 40.)

Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[μgCd g^{-1}] with...				
ln[g cm^2 x10^5]	–0.490	<0.01	Very	
ln[μgCu g^{-1}] with...				
ln[μgPb g^{-1}]	–0.472	<0.01	Very	
ln[μgZn g^{-1}]	0.552	<0.001	Highly	ln[μgCu g^{-1}] = 0.90ln[μgZn g^{-1}] –0.34
ln[g cm^2 x10^5]	–0.540	<0.001	Highly	ln[μgCu g^{-1}] = –1.43ln[g cm^2x10^5] –3.76
ln[μgZn g^{-1}] with...				
ln[g cm^2 x10^5]	–0.719	<0.001	Highly	ln[μgZn g^{-1}] = –1.17ln[g cm^2x10^5] –1.30

The weight per unit area (g cm^{-2}) of the leaves is a measure of the degree of internal consolidation of the leaf structure. This quantity is smallest in the new leaves (collected in October 1987) and reaches a maximum value in the mature leaves (January–March, 1988) (Figure 8·1). (Decreases in the figures for site 5 in the month of April are likely to be due to the leaves shrivelling.)

Concentrations of copper and zinc in horse chestnut leaves are highest in samples collected immediately after the leaves had opened (October 1987) (Figure 8·1). The association of these metals with the growing leaves is likely to be a result of their role in protein and carbohydrate metabolism (section 8·1). Uptake of both metals by plants can be

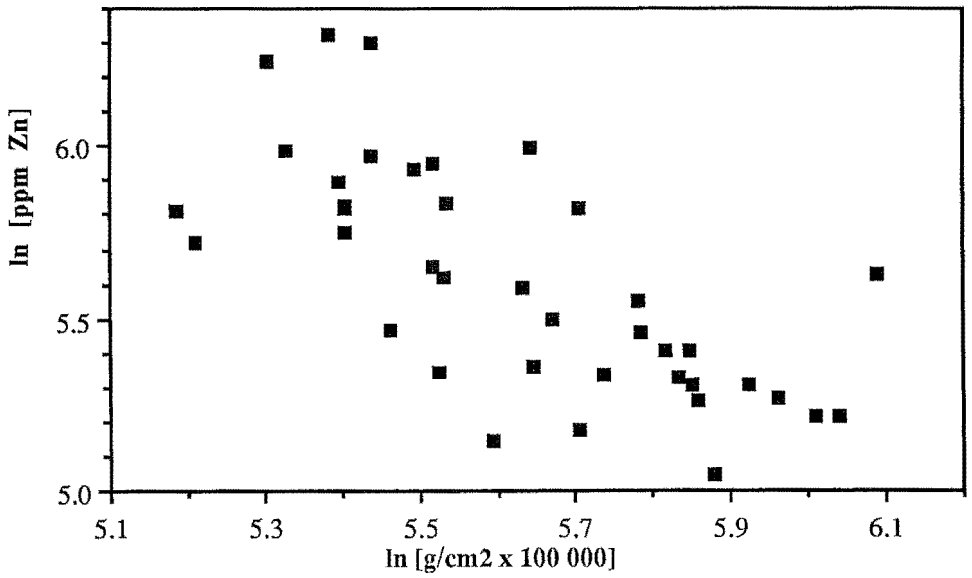
an active process (Kabata-Pendias and Pendias, 1985). A general decrease in copper and zinc concentrations in the leaves occurs with time (Figure 8·1). Comparison of the graphs in Figure 8·1 reveals that the rate of this decrease is the greatest during those months when the weight per unit area of the leaves is increasing the most. The rate of copper and zinc losses reach their minima in mature leaves (January–March). Positive correlations between copper and zinc, and negative correlations between copper and the weight per unit area, and zinc and the weight per unit area are all highly significant (Table 8·6 and Appendix 8·6). These facts suggest the following:

1. Copper and zinc in horse chestnut leaves are mainly derived from the soil (rather than from the atmosphere), as the highest concentrations of these two metals are found in new leaves;
2. Most of the copper and zinc is drawn up to the leaves before they open;
3. Growth of the leaves probably causes dilution of the concentrations of copper and zinc.

The scattergram of the natural logarithm of the zinc concentration versus that of the variable [g cm^{-2} x 10^5] is given in Figure 8·2.

Figure 8·2

Scattergram of the natural logarithm of the ash weight zinc concentrations versus those of the variable g cm^{-2} x 10^5.



Lead concentrations in the leaves show a complete reversal of the trends exhibited by copper and zinc concentrations, and at all sites increase steadily with time (Figure 8·1). The rate of lead accumulation is sufficient to overcome any dilution effect that might be caused by leaf growth. Because each site was within 5 m from a road, the source of the lead in (and/or on) the leaves is likely to be petrol combustion. Lead-rich aerosols may fall directly on the leaves, or may be deposited on the soil, and subsequently leach to the roots. However, it has already been noted that because the amount of lead translocated from the roots to the leaves of plants is minimal, the former enrichment pathway (direct deposition of lead-rich

aerosols from the atmosphere) is likely to predominate (section 8·3·1) (Kabata-Pendias and Pendias, 1985). It is unlikely that the pollutant-trapping effect of Christchurch's thermal-inversion layers (mentioned in Chapter 7) would have any effect on the lead concentrations in the leaves, as thermal-inversions do not usually occur during those months when horse chestnut trees are in leaf (October–April).

Cadmium concentrations in leaves are uncorrelated with those of copper, lead or zinc (Table 8·6 and Appendix 8·6), implying that the primary sources of cadmium (and/or its pathways to the leaf) differ from those of copper, lead and zinc. There is, however, a "very significant" negative correlation between cadmium concentrations in leaves and the weight of the leaves per unit area, which suggests that the growth of horse chestnut leaves does cause a reduction in cadmium levels. Overall, it appears that cadmium concentrations in the leaves may decrease slightly with time, but not to the extent shown by copper and zinc concentrations. (This relationship is discussed further below.) A possible reason that cadmium concentrations in the leaves remain relatively static with time (compared with those of copper, lead or zinc) is that the amount of cadmium drawn into and deposited on each leaf could be such that it effectively compensates for a large part of the (presumed) cadmium dilution caused by leaf growth.

The arithmetic and geometric mean concentrations of each of the variables over all six sites for each month are listed in Appendix 8·7. Graphs of the geometric mean concentrations versus the number of months samples had been collected are given in Figure 8·3.

Figure 8·3
Geometric mean concentrations over the six sites of each variable for each month.

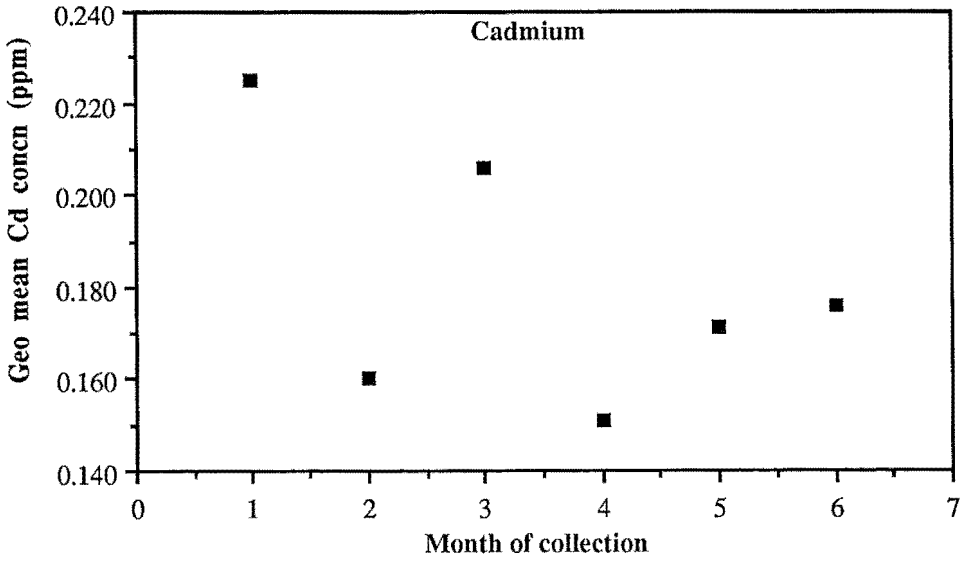
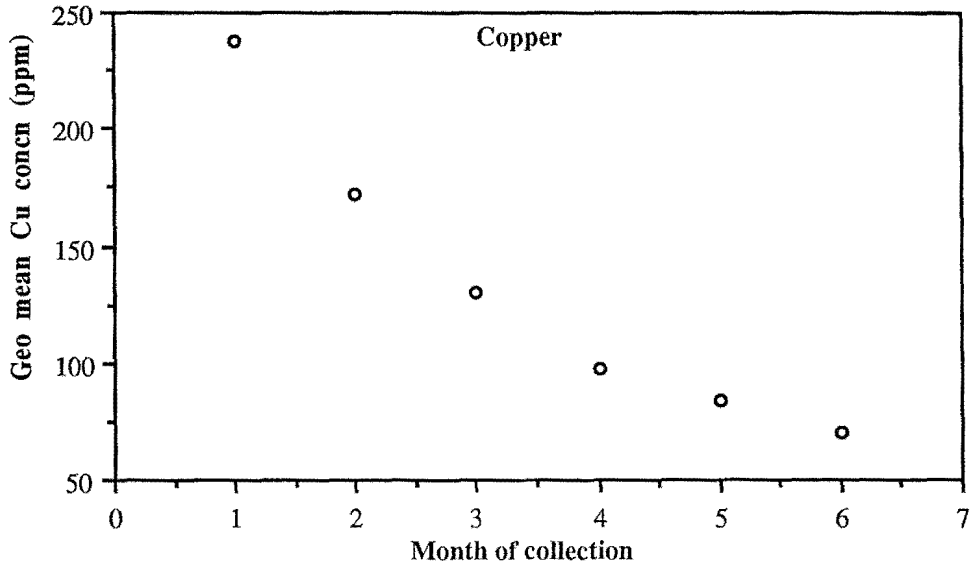


Figure 8·3 continued...



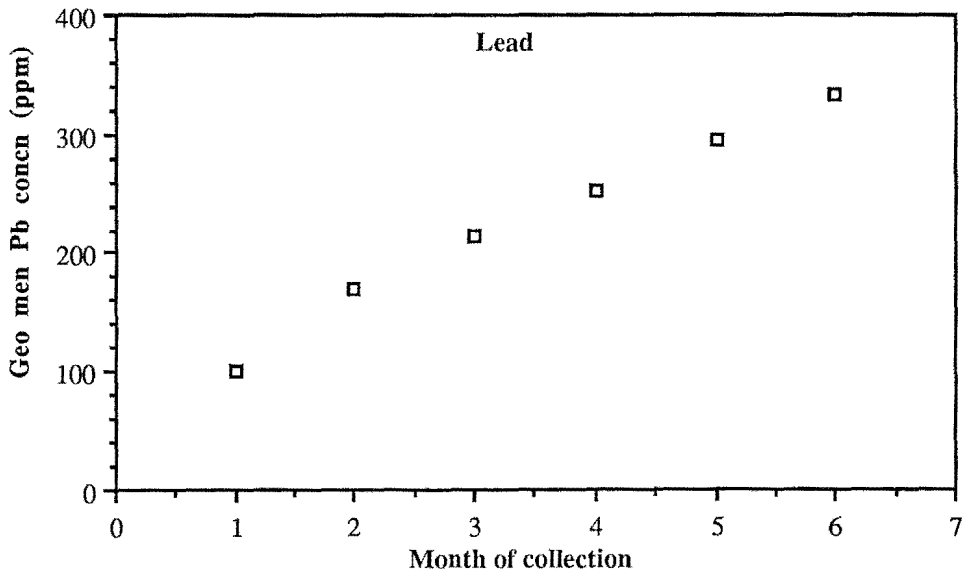
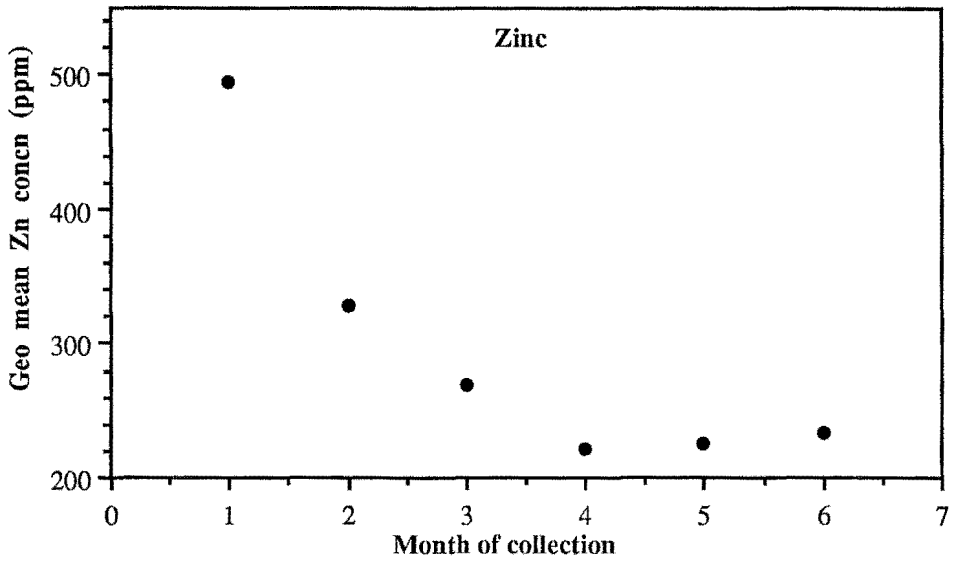
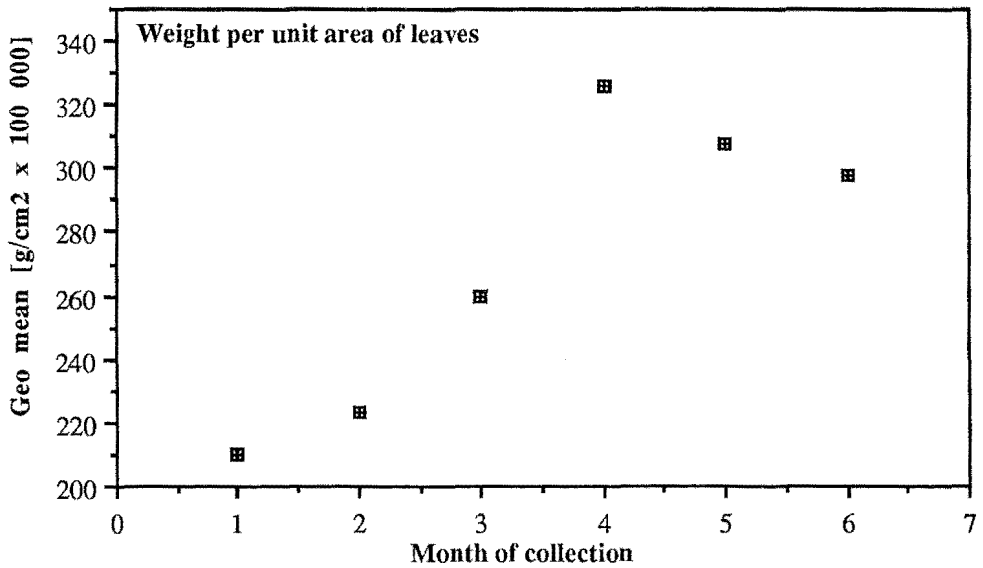


Figure 8·3 continued...





The figures relating to April 1988 were excluded from the calculations, as leaves were only collected from four sites in that month.

Relationships between the number of months that samples had been collected and the monthly (geometric) mean concentrations of the variable [g cm^{-2} x10^5] and the concentrations of copper and zinc in leaves were found to be best described by second degree polynomials (rather than by least-squares lines). This non-linearity may reflect the non-linear nature of leaf growth (and metal dilution).

It should be noted that leaf growth is unlikely to account for all the variation in copper and zinc concentrations. From October 1987 to January 1988, the geometric mean concentrations of copper and zinc in the leaves decreased by 2.43 and 2.23 times (respectively), whereas that of the variable [g cm^{-2} x 10^5] increased by only 1.55 times. Thus, leaf growth could account for a maximum of 64% of the reduction in copper concentrations, and 70% of the decrease in zinc concentrations. It seems likely, then, that some of the copper (especially) and zinc is actively or passively transported out of the leaves once their initial period of rapid growth is finished. In the case of lead, a simple least-squares line best describes the metal's relationship to the number of months samples had been collected. Equations, correlation coefficients and F-test probabilities of these relationships and that of cadmium are given in Table 8·7.

Table 8·7

Equations, correlation coefficients and F-test probabilities of the equations best describing the relationships between the number of months samples had been collected and the weight per unit area, and the month of collection and the concentrations of cadmium, copper, lead and zinc. (Number of pairs = 6.)

Variable	Correl-ation (R)	F-test	Proba-bility (p)	Equation of relationship[a]
µgCd g^{-1}[b]	0.657	1.14	0.428	
µgCu g^{-1}	0.998	492	0.0002	µgCu g^{-1} = 307.89 - 79.26x + 6.71x^2
µgPb g^{-1}	0.993	290	0.0001	µgPb g^{-1} = 45.21 + 69.33x
µgZn g^{-1}	0.989	67.5	0.0032	µgZn g^{-1} = 648.40 - 187.29x + 19.96x^2
10^5[g cm^{-2}]	0.923	8.68	0.057	10^5[g cm^{-2}] = 138.90 + 63.62x + 5.98x^2

Note: **a.** Where x = the number of months samples had been collected (1–6).
b. Second degree polynomial.

Although there is (apparently) a general downward trend in the geometric mean cadmium concentrations with the number of months that samples had been collected (Figure 8·3), this relationship is not statistically significant (Table 8·7). The positive linear relationship between the leaves' geometric mean lead concentrations and the month of collection falls in the "highly significant" category, as do the negative non-linear

relationships between the month of collection and the geometric mean concentrations of copper and zinc. The positive non-linear relationship between the geometric mean weight per unit area of the leaves with the month of collection is "very significant".

8·4 Conclusion

The ash weight geometric mean concentration of cadmium in the horse chestnut leaves sampled is 0.177 $\mu g\ g^{-1}$.

Values of the variable g cm^{-2}, a measure of the maturity of the leaves in terms of the amount of internal consolidation, are lowest in samples collected when the leaves first opened, and increase steadily until January–March. Ash weight concentrations of copper and zinc show the opposite trends, and decrease (in a non-linear manner) with the age of the leaves. Highly significant negative correlations between the variable [g cm^{-2} x 10^5] and the concentrations of copper and zinc suggest that growth of the leaves causes dilution in the concentrations of copper and zinc. Growth of the leaves may account for about 60–70% of the reduction in copper and zinc concentrations with time.

The fact that copper and zinc concentrations are the highest when the leaves first open implies that these metals are primarily derived from the soil (rather than from the atmosphere), and that most of the copper and zinc is drawn into the leaves prior to their unfolding. The association of copper and zinc with developing leaves is probably a result of the roles that these two metals have in plant protein and carbohydrate metabolism.

Ash weight lead concentrations are lowest when the leaves first appear, and increase in a linear (and highly significant) manner with the age of the leaves. The source of this lead is likely to be petrol combustion, and it is probable that direct deposition of the lead-rich aerosols on the leaves (rather than translocation of lead from the roots) is the predominant enrichment pathway. The rate of lead accumulation is sufficient to negate any dilution effect that might be caused by leaf growth. These results complement the positive linear relationship found between the concentration of lead in house-dust and the traffic density in the house-dust survey (section 4·3·3d).

No clear (statistically justified) trend is evident which links cadmium concentrations in horse chestnut leaves with the age of the leaves. Additionally, cadmium concentrations in the leaves are uncorrelated with those of copper, lead or zinc. However, a "very significant" negative correlation between cadmium concentrations and the variable [g cm^{-2} x 10^5] suggests that growth of the leaves may cause some dilution in cadmium concentrations. It is possible that, if cadmium is accumulating on/in the leaves, the rate of this accumulation is sufficient to partially compensate for the dilution effect caused by the leaves growing. Unlike the results for copper, lead and zinc, the results for cadmium do not clearly identify probable sources or enrichment pathways of that metal to leaves. A possible reason for this is that there are several minor sources of cadmium to the leaves, whereas for each of the metals copper, lead and zinc one particular source predominates.

Leaves collected from the three sites situated near main roads (sites 2–4) have statistically more cadmium, copper, and lead than leaves collected from the other sites, implying that traffic is a source of cadmium, copper and lead to horse chestnut leaves.

8·5 References

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8·6 Appendices

Appendix 8·1 (section 8·2·1)

Photographs of one of the bags in position on the branch of an apple tree in the attempted experiment designed to provide a means of differentiating between atmospherically-derived trace metals in/on tree leaves and those derived from other sources.

At the beginning of the experiment...

After three months...

Appendix 8·2 (section 8·3·1)

Ash weight concentrations of cadmium, copper, lead and zinc in horse chestnut leaves collected at monthly intervals from six Christchurch sites. (Each mean value is the average of two measurements. Student's t-test 95% errors are in each case equal to ±6.31 times the standard deviation.)

Location & month	Ash weight metal concentrations ($\mu g\ g^{-1}$)							
	Cadmium		Copper		Lead		Zinc	
	Mean	Std devn	Mean	Std devn	Mean	Std devn	Mean	Std devn
Site 1 (Avon Park)								
Oct 1987	0.288	0.028	333	3	116	4	544	28
Nov 1987	0.125	0.004	214	8	222	16	315	31
Dec 1987	0.234	0.036	121	3	251	6	172	1
Jan 1988	0.148	0.027	97	7	343	21	201	5
Feb 1988	0.146	0.025	70.3	1.1	305	8	155	3
Mar 1988	0.185	0.017	58.0	2.0	518	23	207	4
Apr 1988	0.112	0.008	46.3	2.6	341	6	202	7
Site 2 (Barrington Park)								
Oct 1987	0.442	0.047	197	24	101	15	335	40
Nov 1987	0.326	0.047	142	4	164	6	237	9
Dec 1987	0.489	0.005	144	0	350	1	278	4
Jan 1988	0.305	0.029	96.1	7	239	7	177	3
Feb 1988	0.435	0.040	86.1	5	363	7	275	14
Mar 1988	0.452	0.027	75.5	1.1	448	8	336	3
Site 3 (Erie Monro Playground)								
Oct 1987	0.247	0.019	235	28	191	11	517	44
Nov 1987	0.204	0	196	5	325	18	392	42
Dec 1987	0.321	0.006	147	2	405	32	339	15
Jan 1988	0.148	0.015	125	4	488	33	337	36
Feb 1988	0.141	0.010	91.8	8	426	24	342	16
Mar 1988	0.117	0.009	65.8	4	270	20	268	28
Apr 1988	0.232	0.052	30.3	7	522	68	402	36
Site 4 (Latimer Square)								
Oct 1987	0.173	0.016	173	6	206	14	399	9
Nov 1987	0.147	0.018	132	1	402	7	364	4
Dec 1987	0.152	0.004	113	11	506	58	378	34
Jan 1988	0.153	0.017	85.6	1.5	774	0	285	14
Feb 1988	0.147	0.004	64.7	1.6	748	24	213	6
Mar 1988	0.181	0.021	65.1	4.5	1 100	28	210	17

Appendix 8·2 continued...

Location & month	Ash weight metal concentrations ($\mu g\ g^{-1}$)							
	Cadmium		Copper		Lead		Zinc	
	Mean	Std devn	Mean	Std devn	Mean	Std devn	Mean	Std devn
Site 5 Mahars Road Playground								
Oct 1987	0.191		236		31.5		556	
Nov 1987	0.117	0.014	175	4	58.4	3.7	383	5
Dec 1987	0.162	0.004	101	2	78.5	1.0	244	25
Jan 1988	0.137	0.007	62.9	3.8	97.0	4.2	184	10
Feb 1988	0.161	0.005	62.0	6.3	160	9	222	16
Mar 1988	0.133	0.017	43.3	0.6	138	10	184	12
Apr 1988	0.162	0.007	27.9	15.0	177	1	235	13
Site 6 (University Drive)								
Oct 1987	0.126	0.004	295	11	66.7	3.9	708	16
Nov 1987	0.119	0.001	186	21	86.0	16.6	304	16
Dec 1987	0.084	0.003	169	4	69.8	13.0	257	9
Jan 1988	0.085	0.003	140	2	84.4	3.9	192	3
Feb 1988	0.120	0.008	162	2	118	1	194	10
Mar 1988	0.128	0	154	4	143	19	223	11
Apr 1988	0.113	0.001	132	0	175	4	206	4

Appendix 8·3 (section 8·3·1)

Dry weights per unit area ($g\ cm^{-2} \times 10^5$) of the horse chestnut leaf samples.

Location	Month and year sample collected						
	Oct 1987	Nov 1987	Dec 1987	Jan 1988	Feb 1988	Mar 1988	Apr 1988
Site 1	230	222	269	373	357	310	347
Site 2	179	236	226	300	253	222	
Site 3	201	230	222	300	254	279	282
Site 4	206	221	243	249	283	251	
Site 5	218	249	290	408	336	420	325
Site 6	228	183	324	350	388	346	341

Appendix 8·4 (section 8·3·1)

Mean values (arithmetic and geometric), standard deviations and 95% errors on arithmetic means for each of the tree leaf sampling sites.

	Dry wt of leaves per unit surface area ($g\ cm^{-2} \times 10^5$)	Cadmium ($\mu g\ g^{-1}$)	Copper ($\mu g\ g^{-1}$)	Lead ($\mu g\ g^{-1}$)	Zinc ($\mu g\ g^{-1}$)
Site 1					
Arithmetic mean	301	0.177	134	299	257
Std devn	62	0.064	104	125	137
95% error[a]	±57	±0.059	±96	±115	±126
Geometric mean	296	0.168	107	275	234
Site 2					
Arithmetic mean	272	0.408	123	278	273
Std devn	92	0.074	46	132	61
95% error[a]	±97	±0.078	±48	±139	±64
Geometric mean	261	0.402	117	247	267
Site 3					
Arithmetic mean	253	0.201	127	376	371
Std devn	36	0.072	72	119	78
95% error[a]	±34	±0.066	±67	±110	±72
Geometric mean	250	0.191	107	357	364
Site 4					
Arithmetic mean	242	0.159	106	623	308
Std devn	26	0.015	42	317	84
95% error[a]	±28	0.015	±45	±333	±126
Geometric mean	241	0.158	98.8	547	298
Site 5					
Arithmetic mean	320	0.152	101	106	289
Std devn	76	0.025	76	54	136
95% error[a]	±70	±0.023	±71	±50	±126
Geometric mean	313	0.150	171	91.8	265

Appendix 8·4 continued...

	Dry wt of leaves per unit surface area (g cm^{-2} x 10^5)	Cadmium ($\mu g\ g^{-1}$)	Copper ($\mu g\ g^{-1}$)	Lead ($\mu g\ g^{-1}$)	Zinc ($\mu g\ g^{-1}$)
Site 6					
Arithmetic mean	309	0.111	177	106	298
Std devn	74	0.018	55	40	185
95% error[a]	±69	±0.017	±51	±37	±171
Geometric mean	300	0.109	171	100	266

Note: **a.** Student's t-test error on mean.

Appendix 8·5 (section 8·3·1)

Mean values and confidence errors on means of the ash weight concentrations of cadmium, copper, lead and zinc in leaves and the figure [g cm^{-2} x 10^5] for sites near main roads (sites 2–4) compared with mean values and confidence errors for the other sites.

Variable	Mean		Standard deviation		95% error on mean[a]	
	Sites 2–4	Sites 1, 5 & 6	Sites 2–4	Sites 1, 5 & 6	Sites 2–4	Sites 1, 5 & 6
$\mu gCd\ g^{-1}$	0.253	0.146	0.123	0.048	±0.060	±0.022
$\mu gCu\ g^{-1}$	209	137	152	84	±73	±38
$\mu gPb\ g^{-1}$	422	170	242	121	±117	±55
$\mu gZn\ g^{-1}$	320	280	82	148	±40	±67
g cm^{-2} x 10^5	294	310	95	68	±46	±31

Note: **a.** Student's t-test error on mean.

Appendix 8·6 (section 8·3·2)

Correlation matrix for the variables in the horse-chestnut leaves survey. Number of pairs = 40.

	$\ln[\mu gCd\ g^{-1}]$	$\ln[\mu gCu\ g^{-1}]$	$\ln[\mu gPb\ g^{-1}]$	$\ln[\mu gZn\ g^{-1}]$	$\ln[g\ cm^{-2}x10^5]$
$\ln[\mu gCd\ g^{-1}]$	1				
$\ln[\mu gCu\ g^{-1}]$	0.064	1			
$\ln[\mu gPb\ g^{-1}]$	0.089	–0.472	1		
$\ln[\mu gZn\ g^{-1}]$	0.203	0.552	–0.190	1	
$\ln[g\ cm^{-2}x10^5]$	–0.490	–0.540	–0.029	–0.719	1

Appendix 8·7 (section 8·3·2)

Monthly arithmetic and geometric mean concentrations of each variable over all six sites, and standard deviations and 95% confidence errors (Student's t-test) for the arithmetic means.

	Oct 1987	Nov	Dec	Jan	Feb	Mar	Apr 1988
Number of sites	6	6	6	6	6	6	4
$\mu gCd\ g^{-1}$							
Arithmetic mean	0.245	0.173	0.240	0.163	0.192	0.199	0.155
Standard deviation	0.112	0.082	0.146	0.074	0.120	0.127	0.057
95% error on mean	±0.101	±0.074	±0.132	±0.067	±0.108	±0.114	±0.077
Geometric mean	0.225	0.160	0.206	0.151	0.171	0.176	0.147
$\mu gCu\ g^{-1}$							
Arithmetic mean	245	174	133	101	89.5	85.2	59.1
Standard deviation	60	32	25	28	37.5	38.6	49.3
95% error on mean	±54	±29	±23	±25	±33.8	±34.8	±67.0
Geometric mean	238	172	130	97.9	84.4	70.7	47.7
$\mu gPb\ g^{-1}$							
Arithmetic mean	119	210	277	338	353	436	304
Standard deviation	69	135	177	263	226	360	165
95% error on mean	±62	±122	±160	±237	±204	±324	±224
Geometric mean	99.5	170	215	252	296	333	272
$\mu gZn\ g^{-1}$							
Arithmetic mean	510	333	278	229	234	238	261
Standard deviation	131	59	73	66	66	55	95
95% error on mean	±118	±53	±66	±59	±59	±49	±129
Geometric mean	495	328	270	222	226	233	250
$[g\ cm^{-2} \times 10^{5}]$							
Arithmetic mean	210	224	262	330	312	305	324
Standard deviation	19	22	40	58	57	71	29
95% error on mean	±20	±23	±42	±60	±59	±75	±47
Geometric mean	210	223	260	326	308	298	323

CHAPTER 9
SEASONAL VARIATIONS IN THE CONCENTRATIONS OF DISSOLVED CADMIUM, COPPER, LEAD AND ZINC IN THE AVON AND HEATHCOTE RIVERS, CHRISTCHURCH.

9·1 Introduction

The main sources of trace metals to natural waters are runoff from weathering processes, industrial and domestic wastes, fallout of airborne particulates (wet or dry), and degradation of plant and animal tissue (Eichenberger and Chen, 1982).

Trace metals in rivers exist both in particulate and in dissolved forms. Particulate metals are defined for experimental purposes as those metallic species which are retained by a 0.45 μm (membrane) filter. Species of this size and above are generally regarded as being unavailable to fish gills (Florence and Batley, 1977). Conversely, dissolved metals—defined for the purposes of experiment as those metallic species which pass through a 0.45 μm filter—are generally regarded as being "fish-gill accessible". (Reference to particulate and dissolved metal fractions will be in accordance with the above definitions throughout this Chapter.)

Cadmium dissolved in natural waters can be complexed by organic and/or inorganic ligands, or simply exist as the "free" (aquocomplexed) divalent cation (Cd^{2+}) (Van Leeuwen, 1979). Particulate forms of cadmium include those where cadmium has been adsorbed onto solid surfaces, chemically bound to organic matter, incorporated into organisms, or has formed part of a solid precipitate (Khalid, 1980). Particulates and bottom sediments tend to act as scavengers of dissolved cadmium, and usually contain significantly higher concentrations of the metal than the dissolved phase (Horowitz, 1985; Khalid, 1980).

The mobility, bioavailability and ultimate toxicity of dissolved cadmium is dependent to a large extent on its chemical species (Florence, 1982; Khalid, 1980). The free metal ion (Cd^{2+}), and species which are lipid-soluble (and can thus pass unhindered through biomembranes) are regarded as being the most toxic forms of cadmium in natural waters (Florence, 1988).

Speciations of dissolved cadmium, and the (dynamic) equilibrium which exists between the fraction of total cadmium associated with the dissolved phase and that held by the particulates and bottom sediments, are influenced by a number of factors. These include redox potential, pH, ionic strength, salinity, the type and concentration of potential ligands and of competing metals, the availability and quantity of adsorptive surfaces, and the actual concentrations of cadmium in the dissolved and particulate phases (Ahrland, 1988; Braman, 1983; Eichenberger and Chen, 1982; Khalid, 1980; Laxen, 1983; Weber and Posselt, 1976).

Christchurch city is drained by two rivers: the Avon River and the Heathcote River. These are shown in Appendix 3·1 (inside back cover). Both rivers are primarily spring-fed, originate to the west, and eventually flow into the Avon-Heathcote Estuary (in the east).

Tidal variations influence the water levels in both rivers to about 12 km upstream (Anon. 1988).

The Avon River is 26 km in length, has eight natural tributaries of significance, and enters the Avon-Heathcote Estuary at a low-flow rate of about 2.7 $m^3 s^{-1}$ (Anon. 1988). At one point it flows through the inner city.

The Heathcote River is 22 km long, has only one tributary of significance, and flows more slowly than the Avon River—entering the Avon-Heathcote Estuary at a low-flow rate of about 0.88 $m^3 s^{-1}$ (Anon. 1988). Rural areas comprise a substantial portion of its catchment. Factories are located on the Heathcote River's banks in the suburb of Woolston (in particular), and a considerable amount of industrial waste has been discharged directly into the river in the past (see, for instance, Purchase, 1983). Nowadays, waste from the factories on the Heathcote River's banks is fed into the sewage system.

This study was designed to monitor seasonal variations in the concentrations of dissolved cadmium, copper, lead and zinc in the Avon and Heathcote Rivers.

9·2 Method

9·2·1 Sample selection, collection and processing

The Avon and Heathcote Rivers (Christchurch) were the focus of this study. Water samples were collected at low tide from six widely spaced sites along most of the lengths of each river, monthly for 12 consecutive months. The sampling sites are shown in Appendix 3·1. Water was not sampled from points any further downstream than the Bassett Street Bridge (Avon River) or the Catherine Street Bridge (Heathcote River), in order to avoid potential problems associated with the GFAAS and FAAS analysis of saline water samples, such as molecular absorption in the FAAS flame by sodium chloride, or complexation of cadmium by chloride ions (Pruszkowska *et al.* 1983). The actual sampling dates were 23 July 1987, 21 August 1987, 22 September 1987, 23 October 1987, 23 November 1987, 21 December 1987, 22 January 1988, 19 February 1988, 25 March 1988, 20 April 1988, 26 May 1988 and 20 June 1988.

Water samples were collected in 270 ml polypropylene bottles. Before sample collection, the bottles were soaked in 4 M AR nitric acid for (at least) 48 hr, rinsed several times with double-distilled water, and rinsed once more with river water (at a point downstream from the collection site). Plastic disposable gloves were used when collecting the water samples, which were taken upstream from the bottle-holding hand, at a water depth of 10 cm, and at a distance from the river-bank of about 1 m. Water temperature (at a depth of 10 cm) was measured by thermometer at each site after sample collection. The pH of a small (and later discarded) portion of each sample was measured later in the laboratory using an electronic pH-meter (calibrated against phosphate buffer of pH 6.85).

Immediately after collection, in a class 100 Clean Room, 250 ml of each sample was filtered through a nitric acid and double-distilled water washed membrane filter of pore-size

0.45 µm (Millipore). The filtered samples were transferred to a clean 500 ml round-bottomed flasks, frozen, and freeze-dried (Alpha I/5, Martin Christ).

Freeze-drying, which is an evaporation technique, is achieved using a vacuum of sufficient strength to cause the material being dried to assume a temperature of less than −10 °C. Under these conditions, ice sublimes directly to water vapour. Freeze-drying has been shown to be as effective as solvent extraction or chelating ion exchange for the concentration of cadmium from fresh water samples (Hall and Godhino, 1980). Advantages of using freeze-drying as a method of preconcentration in this study included the following:

1. All the metals in the sample were concentrated simultaneously,
2. Volatile species were more likely to be retained,
3. The potential for contamination of samples during the concentration step by impurities in the solvents was eliminated.
4. The freeze-dried products were water-soluble.

No obvious salt was evident in the freeze-dried samples. After each sample was freeze-dried, the material remaining in the 500 ml round-bottomed flask was dissolved in 5 ml of warm 4 M nitric acid, and transferred to a 10 ml volumetric flask. Residual acid was rinsed from the interior of the round-bottomed flask (and into the volumetric flask) with small amounts of double-distilled water, until the concentrated sample solution reached a volume of 10 ml (thus preconcentrating the original sample 25 times).

Christchurch climatological data for the dates that samples were collected was purchased from the New Zealand Meteorological Service.

9·2·2 Analysis of preconcentrated samples

The preconcentrated river water samples were analysed for cadmium by GFAAS (on peak-area mode, with deuterium background correction) using the furnace heating program given in Table 9·1.

Table 9·1

GFAAS furnace heating program for the measurement of cadmium in preconcentrated river water samples.

Step number	Step	Temperature (°C)	Ramp time (s)	Holding time (s)
1	Drying # 1	80	3	1
2	Drying # 2	122	2	1
3	Ashing	420	2	10
4	Atomization	2 000	2	1

Other parameters of the GFAAS analysis of cadmium are given in Chapter 14.

Zinc concentrations in preconcentrated water samples were determined by FAAS. Samples collected in July and August 1987 were analysed for copper and lead using FAAS.

However, samples collected after August 1987 were analysed for copper and lead by GFAAS, as lower detection limits were desirable. (Parameters relating to the FAAS analysis of zinc, and the FAAS and GFAAS analyses of lead and copper are given in Chapter 14.)

Standards were prepared from 1 000 μg ml^{-1} stock solutions, and given the same acid-strength as the samples. Blanks comprised AR nitric acid diluted with double-distilled water.

Taking into account the preconcentration factor, the experimental limits of detection for cadmium, copper and lead (when analysed by GFAAS) and zinc (FAAS) in the river water samples were approximately 0.007, 0.08, 0.1 and 1 μg l^{-1}, respectively. The method of standard additions revealed that no significant interferences were present in the analyses of cadmium, copper, lead or zinc.

The DSIR coordinates an ongoing water analysis inter-laboratory comparison programme in New Zealand, which is known as *Chemaqua*, (Mattingly, 1988). "Round 13" of Chemaqua consisted of two water samples; both of these were analysed by the above methods for cadmium, copper, lead and zinc. The results are listed alongside those of other laboratories in Table 9·2.

Table 9·2

Comparison of the concentrations of cadmium, copper, lead and zinc in two water samples determined in this study with the concentrations determined by other laboratories for the same two samples (Chemaqua, Round 13).

	Other laboratories				This study	
	Number of laboratories	Number below limit of detection	Median concn	Range	Concn determined	Estimated[a] recovery (%)
Cadmium (μg l^{-1})						
Sample # 1	9	6	[b]	<4	0.13	
Sample # 2	9	6	[b]	<4	0.26	
Copper (μg ml^{-1})						
Sample # 1	26	16	0.010[c]	0.000–0.100	0.074	
Sample # 2	22	1	0.33	0.00-0.43	0.342	104
Lead (μg ml^{-1})						
Sample # 1	13	11	[b]	<0.1	0.019	
Sample # 2	13	0	0.37	0.06–0.46	0.372	101
Zinc (μg ml^{-1})						
Sample # 1	23	1	0.090	0.040–0.130	0.123	137
Sample # 2	23	1	0.31	0.28–0.35	0.314	101

Notes: **a.** Taken here as 100[concentration determined in this study/median of other laboratories].
b. Insufficient positive data for median estimation to be made (by the DSIR).
c. Median regarded as unreliable by the DSIR, due to the high number of observations which fell below the detection limit.

The concentrations of copper, lead and zinc determined in this study are quite close in value to those of the median concentrations of the three metals determined by other laboratories which can be estimated and which are considered to be reliable (Table 9·2). Unfortunately, because of the comparatively low absolute concentrations of cadmium in the two samples (or to the insensitivities of the analytical techniques used by the other laboratories), likely median cadmium concentrations could not be calculated by the DSIR. However, the favourable results for copper, lead and zinc would tend to imply that the cadmium concentrations determined in this study are also likely to be reasonably close in value to the "true" concentrations of the metal in the two samples.

9·2·3 Methodology for speciations studies

The dielectric constant of n-octanol ($CH_3(CH_2)_6CH_2OH$) is regarded as being close in value to that of a lipid membrane, and the solubility of a given metal in n-octanol has been used to estimate that metal's solubility in biomembranes (Florence, 1988). Solubility in n-octanol is thus related to toxicity. (For instance, the solubilities of copper oxime complexes in n-octanol have been found to correlate reasonably well with their toxicity to algae (Florence, 1988).)

An estimate of the *lipid-soluble* fraction of dissolved cadmium, copper, lead and zinc in Avon River water was made as follows. Four 500 ml water samples were collected from sites along the Avon River on 21 April 1989. Each of these was filtered through a 0.45 μm Millipore membrane filter, and then divided into two 250 ml aliquots. One of these was shaken with 100 ml of vacuum-distilled n-octanol in a separating-funnel. The mixture was left to stand for 24 hr, after which time the aqueous phase was recovered. Both sub-samples were then frozen, preconcentrated by freeze-drying, and analysed for cadmium, copper and lead by GFAAS, and for zinc by FAAS (as in section 9·2·2).

Anodic Stripping Voltammetry (ASV) was used for further studies in the speciations of dissolved cadmium in Avon River water. Because ASV is a non-equilibrium technique, the concentration of a given metallic species in solution as determined by ASV does not necessarily reflect the true equilibrium concentration of that species (Brezonik *et al.* 1976; Florence and Batley, 1980; Skogerboe *et al.* 1980; Van Leeuwen, 1979 and 1987). Despite this limitation, it has been found that in general, a positive relationship usually exists between the toxicity of a given metal in water to aquatic organisms and the proportion of that metal (operationally) defined as "ASV labile" (Florence, 1988). The technique of ASV is further described in Chapter 14.

Six 250 ml water samples were collected from the same site on the Avon River (McBratneys Road area) on 27 April 1989. These were filtered firstly through a (Millipore) membrane filter of pore size 0.45 μm (in order to remove particulate matter) and subsequently through a membrane filter of pore size 0.025 μm (to remove colloidal material). This second filtering step was carried out because earlier ASV trial-runs, using water filtered at 0.45 μm only, had failed; this was thought to be a result of accumulation of colloidal material on the reference electrode (Powell, 1988).

Three 50 ml aliquots were taken from each sample, and treated according to a modified version (obtained from Florence, 1988) of the method devised by Florence and Batley (1979).

This involved the following steps:

1. To the first 50 ml aliquot, 500 µl of 2 M sodium acetate/acetic acid buffer was added (giving a final solution pH of 4.8). The purpose of the buffer was to provide electrolytes for facilitation of the electrolytic reactions.
2. The second 50 ml aliquot was placed in a silica tube. Hydrogen peroxide (50 µl) was added, and the tube was irradiated with light from a 500 W ultra-violet lamp (at a distance of 5 cm) for 8 hr. This procedure was designed to destroy organic matter (and thus liberate organically-bound metallic species). After irradiation, 500 µl of the 2 M sodium acetate/acetic acid buffer was added to this sub-sample.
3. The third 50 ml aliquot was also placed in a silica tube, and after addition of 63 µl of concentrated AR nitric acid and 50 µl of hydrogen peroxide, was also irradiated with ultra-violet light (using the same conditions as were used for the second aliquot). The purpose of this procedure was to liberate both organically and inorganically bound metallic species.

The three sub-samples were analysed for cadmium by ASV on differential pulse mode. The ASV operating parameters used in this study are listed in Table 9·3.

Table 9·3

Parameters used in the ASV determination of various species of cadmium and lead in Avon River water.

Parameter	Value, *etc.*
Make and model	Princeton Applied Research, Model 303
Mercury drop	Static
Operating mode	Differential pulse
Initial potential	–0.8 V
Deposition time	20 min
Current range	0.02 to 0.5 µA
Modulation amplitude	25 mV
Scan rate	5 mV s^{-1}

Cadmium's half-wave potential appeared at –0.6 V. Calibration curves were constructed by the method of standard additions. Blanks corresponding to each aliquot were prepared from double-deionized (Milli-Q) water and the appropriate reagents (in the appropriate proportions).

Concentrations of cadmium determined by ASV in the first aliquot represented the "ASV labile" fraction of the metal. Concentrations determined in the second aliquot were taken to represent the "ASV labile and organically bound" fractions, and those determined in the third aliquot were taken to represent the total cadmium in the samples (*i.e.* labile,

organically bound and inorganically bound cadmium) (Florence and Batley, 1977; Florence, 1988).

9·3 Results and discussion

9·3·1 Summary statistics

Appendix 9·1 is a complete list of monthly means, standard deviations and medians of the concentrations of dissolved cadmium, copper, lead and zinc, and of the pH, in samples of Avon and Heathcote River water. (Each mean or median is that relating to the six sampling sites along each river.) Values of the variables "water temperature", "air temperature", "rainfall" and "mean wind speed" applicable to each day that samples were collected are also given in Appendix 9·1. Summary statistics derived from the monthly median concentrations of dissolved cadmium, copper, lead and zinc, the median values of the pH, and water temperatures over both rivers (n = 24) are presented in Table 9·4.

Table 9·4

Overall summary statistics of the median concentrations ($\mu g\ l^{-1}$) of cadmium, copper, lead and zinc, median pH values, and the water temperatures in the survey of Avon and Heathcote River water (n = 24).

Variable	Arithmetic mean	Standard deviation	95% error on mean[a]	Geometric mean	Range Lowest	Range Highest
Cd concn ($\mu g\ l^{-1}$)	0.16	0.11	±0.05	0.14	0.06	0.51
Cu concn ($\mu g\ l^{-1}$)	2.6	2.9	±1.2	1.9	0.6	14.8
Pb concn ($\mu g\ l^{-1}$)	4.3	4.0	±1.7	2.5	0.4	12.6
Zn concn ($\mu g\ l^{-1}$)	53	62	±26	39	13	320
pH	7.50	0.27	±0.11	7.50	6.97	8.10
Water temp (°C)	14.3	3.7	±1.6	13.8	9.0	19.5

Note: **a.** Student's t-test.

Data describing cadmium concentrations in samples collected on 22 September 1987 from the Avon and Heathcote Rivers were identified as outliers (by the method of Grubbs, 1969) and were not included in the calculations of summary statistics. Although the extremely high cadmium concentrations represented by these outliers could have been caused by real increases in cadmium levels in the Avon and Heathcote Rivers on the dates concerned, it was thought to be more likely that the samples had been contaminated by cadmium during processing, digestion, or analysis. Analysed concentrations of cadmium in some of the samples collected on 22 September 1987 were quite low, whereas levels determined in others were very high. Moreover, some of the sampling sites from which

water containing low levels of cadmium was collected were between two sites from which water with (apparently) high cadmium concentrations had been gathered. If there had been real increases in the Avon and Heathcote Rivers' cadmium concentrations, it would be expected that high concentrations of cadmium would be found in samples from consecutive sites. Additionally, no obvious source of cadmium contamination was evident.

The means of the coefficients of variation of the monthly median concentrations of cadmium, copper, lead and zinc in Avon and Heathcote River water samples are 43%, 61%, 36% and 59%, respectively. These figures are relatively high, and represent real variations in the levels of each metal between the six sampling sites located along each river superimposed upon random analytical variations.

The geometric mean levels of dissolved cadmium, copper, lead and zinc given in Table 9·4 probably represent "typical" concentrations more accurately than the arithmetic means, as the four metals' data sets are positively skewed (Appendix 9·1). The overall geometric mean cadmium concentration (calculated from the 24 monthly median values) is 0.14 $\mu g\ l^{-1}$, and the range is 0.06–0.51 $\mu g\ l^{-1}$.

Geometric mean concentrations of dissolved cadmium, copper, lead and zinc found in Avon and Heathcote River water samples in this study are compared with the levels of these metals usually found in the world's "unpolluted" freshwaters, concentrations more typical of industrialized areas, and concentrations reported to be typical of the Upper Manuherikia River (New Zealand) in Table 9·5. Concentrations of metals in the Upper Manuherikia River (located in a remote area of Central Otago) could be taken as background concentrations for New Zealand rivers (Ahlers and Hunter, 1984 and 1988).

Table 9·5

Comparison of geometric mean concentrations of cadmium, copper, lead and zinc in Avon and Heathcote River water samples with New Zealand background concentrations and with levels typical of the world's "unpolluted" and "industrial" freshwaters.

Metal	Concentration ($\mu g\ l^{-1}$) typically found in...			This study	
	Unpolluted freshwaters[a]	Freshwaters in industrial areas[a]	Upper Manuherikia River (N.Z.)[b]	Geo mean concn ($\mu g\ l^{-1}$)	Enrichment *c.f.* N.Z. background
Cadmium	0.010–0.100	<0.5	0.010	0.14	14
Copper	0.5–1.0	≥3	0.15	1.9	13
Lead	≤3	≤60	0.03	2.5	83
Zinc	0.5–15	≤100	0.15	39	260

Notes: **a.** Moore and Ramamoorthy, 1984.
b. Ahlers and Hunter, 1988; taken to represent background levels in New Zealand riverwater.

The geometric mean concentrations of dissolved cadmium, copper, and zinc in Avon and Heathcote River water samples are all higher than levels cited as typical of the world's unpolluted freshwaters, but lower than concentrations often found in rivers in industrialized areas (Table 9·5). Geometric mean lead concentrations in Avon and Heathcote River water samples are within the range quoted for the world's unpolluted freshwaters.

However, geometric mean concentrations of all four metals are considerably higher than the "New Zealand background" concentrations (found in the Upper Manuherikia River) (Table 9·5). Enrichment factors for the metals in the Avon and Heathcote Rivers (with respect to concentrations in the Upper Manuherikia River) are in the order zinc (260) > lead (83) > cadmium (14) > copper (13). Although some of the enrichment could be due to dissimilarities in the geological characteristics of the watershed areas of Christchurch and Central Otago (Abdullah and Royle, 1972), it seems probable that Christchurch's urbanization is the chief reason why concentrations of cadmium, copper, lead and zinc are (comparatively) high in the Avon and Heathcote Rivers. Additionally, because rural areas comprise a large part of the catchment of the Heathcote River (section 9·1), farming practices (such as fertilizer application) could influence the levels of some trace metals in that river.

Weathering of galvanized-iron roofing and combustion of petrol-lead are two sources which more or less uniquely emit zinc and lead (respectively) and which are found mainly in the urban environment. As such, they may be responsible for the extremely high enrichment (over background) factors of lead and zinc in the Avon and Heathcote Rivers.

Summary statistics of the data relating to each river are presented in Table 9·6.

Table 9·6

Summary statistics of the median concentrations (μg l^{-1}) of cadmium, copper, lead and zinc, median pH values, and the water temperatures for each river.

Variable	Arithmetic mean	Standard deviation	95% error on mean[a]	Geometric mean	Range Lowest	Range Highest
Avon River						
Cd concn (μg l^{-1})	0.15	0.10	±0.07	0.13	0.06	0.39
Cu concn (μg l^{-1})	1.8	1.0	±0.6	1.6	0.7	4.0
Pb concn (μg l^{-1})	4.3	4.0	±2.5	2.6	0.4	12.6
Zn concn (μg l^{-1})	35	21	±14	30	13	80
pH	7.41	0.25	±0.16	7.40	6.97	7.83
Water temp (°C)	14.5	3.9	±2.9	13.9	9.0	19.5
Heathcote River						
Cd concn (μg l^{-1})	0.18	0.12	±0.08	0.15	0.08	0.51
Cu concn (μg l^{-1})	3.3	3.8	±2.5	2.2	0.6	14.8
Pb concn (μg l^{-1})	4.2	4.1	±2.6	2.5	0.4	12.4
Zn concn (μg l^{-1})	70	83	±52	50	15	320
pH	7.60	0.26	±0.08	7.60	7.10	8.10
Water temp (°C)	14.1	3.5	±2.2	13.7	9.0	18.0

Note: **a.** Student's t-test.

A two-tailed paired t-test (by computer) showed that there were no significant differences (at a 95% confidence level) between the concentrations of dissolved cadmium, copper, lead and zinc in the Avon River samples and those in samples from the Heathcote River. Interestingly, water samples from the Avon River are statistically more acidic (mean pH 7.41) than Heathcote River samples (mean pH 7.60) (single-tailed t-test probability: 99.65%).

9·3·2 Correlations and monthly variations

Graphs showing monthly variations in water temperatures of the Avon and Heathcote Rivers (measured on the days that samples were collected), and variations in the medians of the pH and the concentrations of dissolved cadmium, copper, lead and zinc in Avon and Heathcote River water samples, are given in Figure 9·1 (which is derived from the data in Appendix 9·1). The correlation matrix relating to all variables is given in Appendix 9·2. The data sets of the metal concentrations and that of the variable "water temperature" were approximately log-normal; observations in these data sets were therefore transformed to their natural logarithms prior to the derivation of the correlation matrix. Significant correlations between variables (everything with $p<0.05$) are listed in Table 9·7. As an aid to visualization of interrelationships between variables, a dendogram constructed from the correlation matrix is presented in Figure 9·2.

Figure 9·1

Monthly variations in the concentrations ($\mu g\ l^{-1}$) of dissolved cadmium, copper, lead and zinc in, and the pH and water temperature of, Avon and Heathcote River water samples. Note: graphs are for the period July 1987 to June 1988; the graphed value of each variable (except "water temperature") for each month is the median of six values; two outliers are plotted as zero in the case of cadmium (September 1987); two values less than the detection limit are plotted as zero in the case of lead (August, 1987).

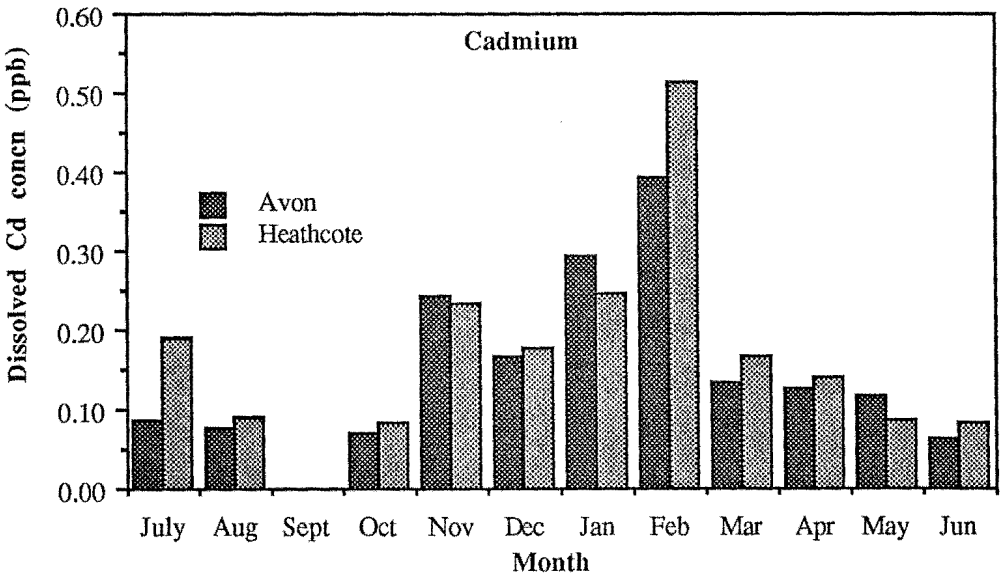
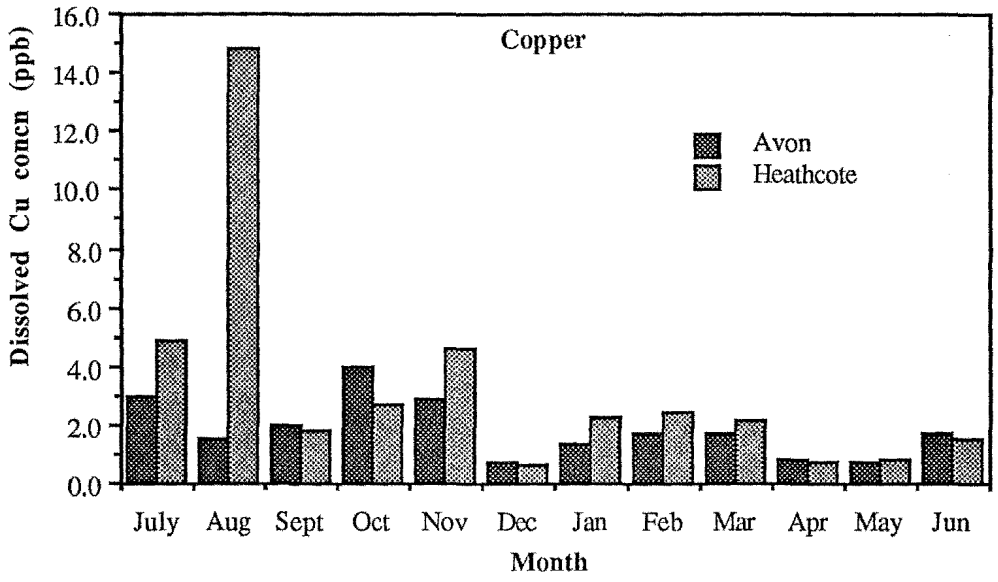


Figure 9·1 continued...



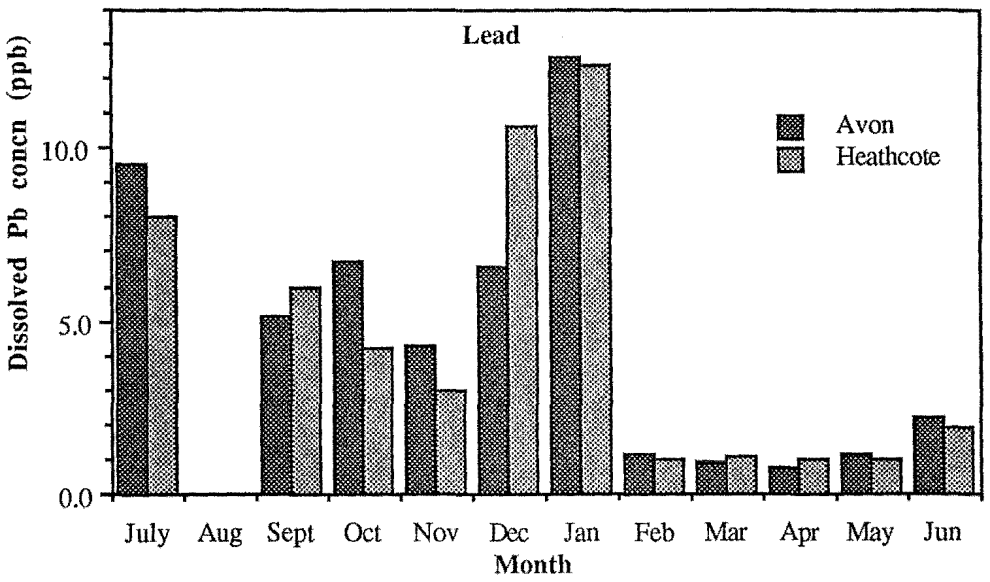
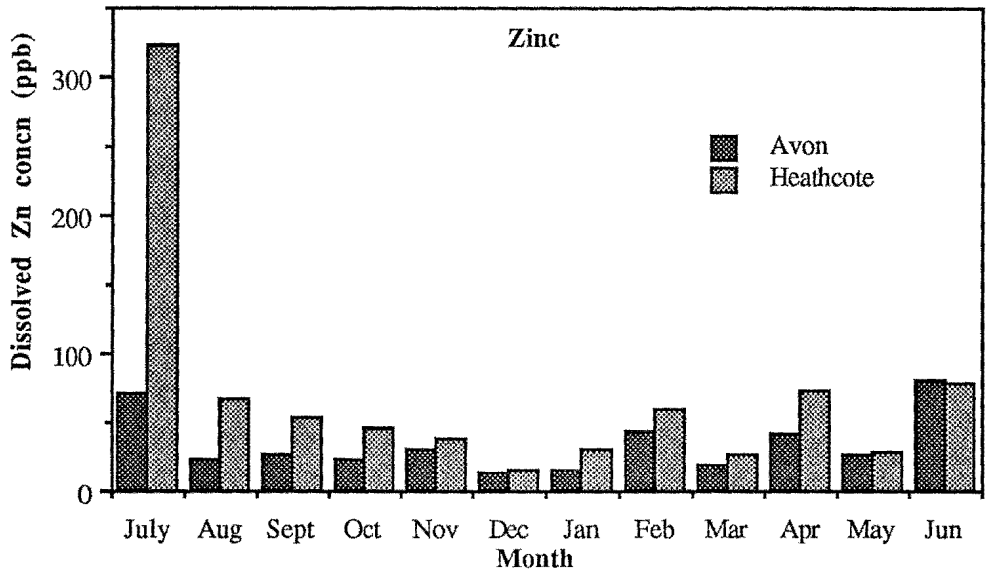


Figure 9·1 continued...



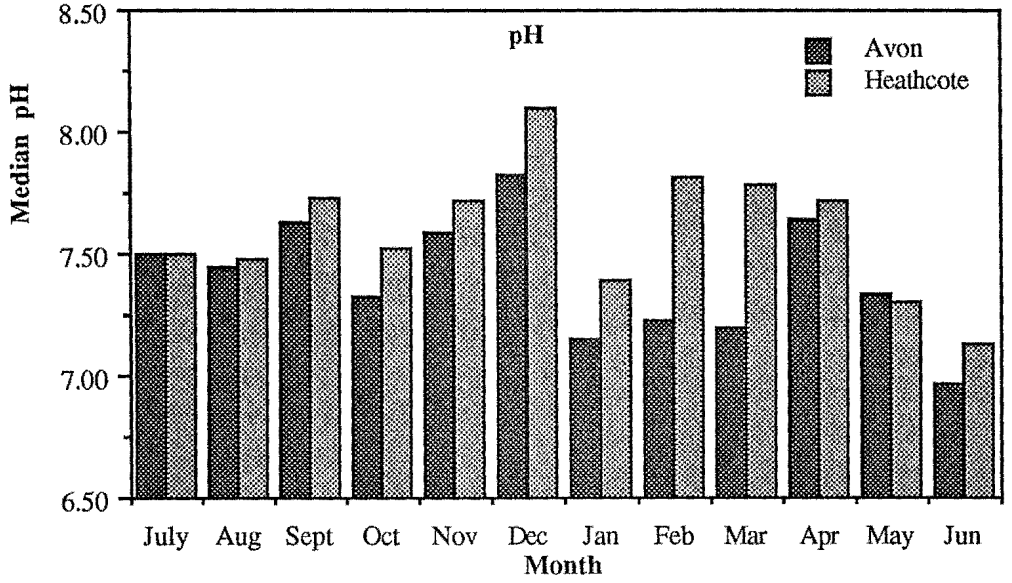


Figure 9·1 continued...

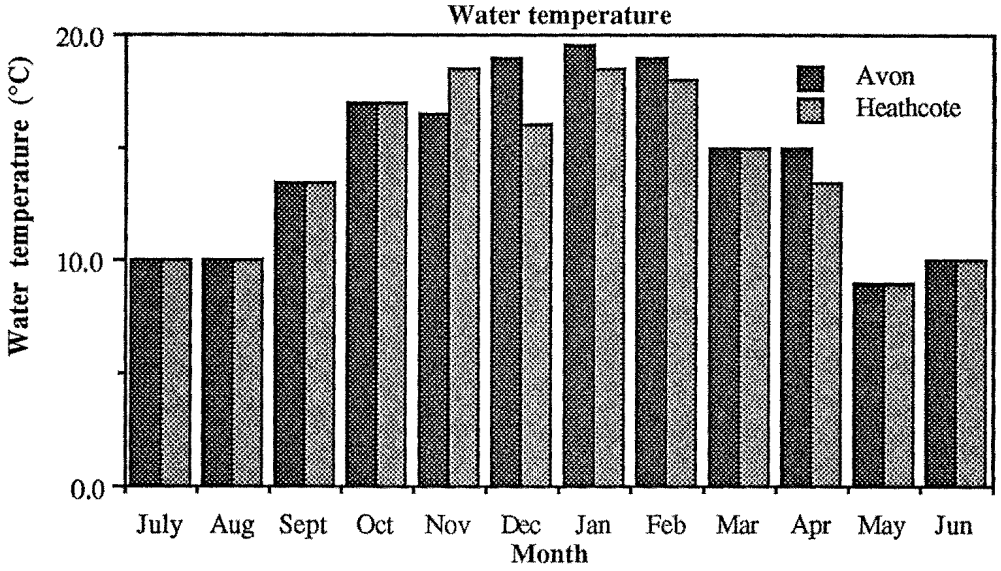


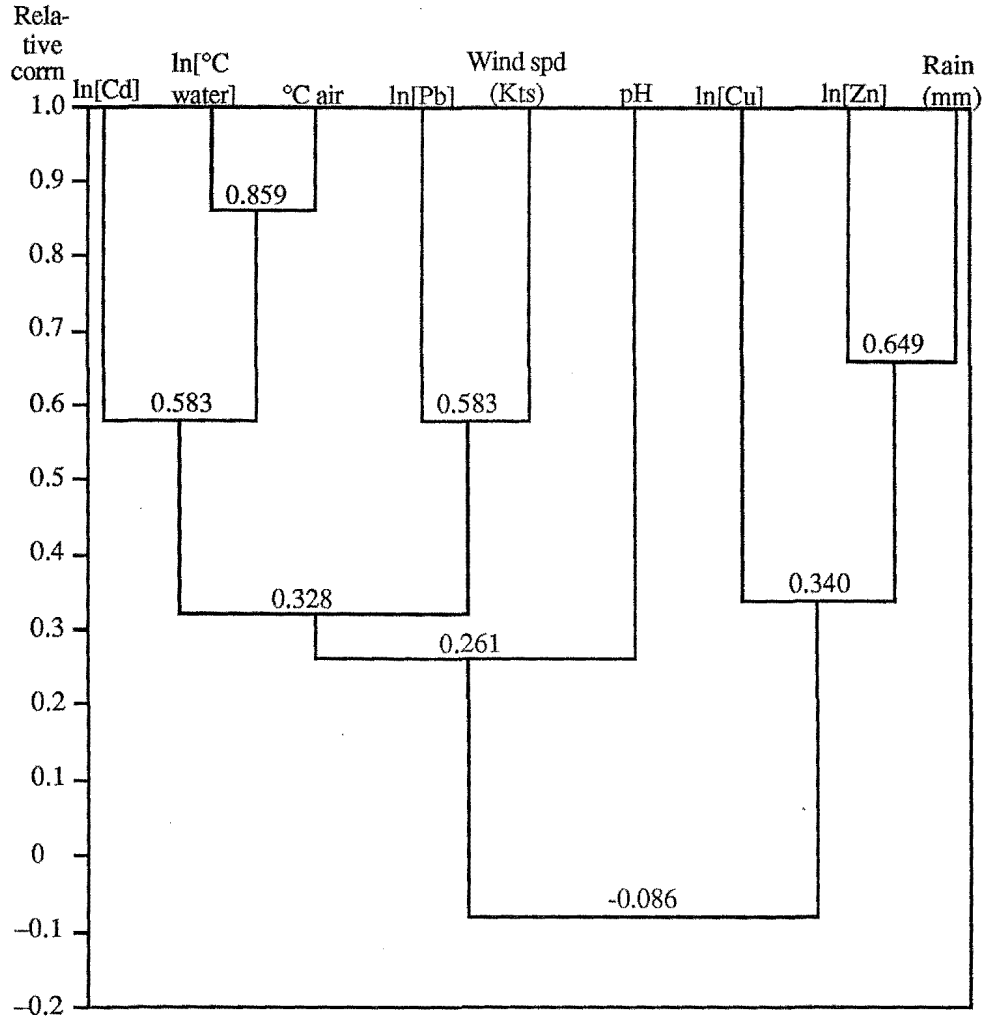
Table 9·7

Significant correlations between the variables in the Avon and Heathcote River water survey. Least-squares equations are given in the two cases where the correlation is highly significant. (Number of data pairs = 24).

Correlated pair	Correlation coefficient	Probability (p)	Significance	Least-squares relationship
ln[µgCd l^{-1}] with...				
ln[Water temp (°C)]	0.625	<0.01	Very	
Air temp (°C)	0.541	<0.01	Very	
Wind speed (Kts)	0.534	<0.01	Very	
ln[µgCu l^{-1}] with...				
ln[µgZn l^{-1}]	0.432	<0.05	Just	
ln[µgPb l^{-1}] with...				
Wind speed (Kts)	0.583	<0.01	Very	
ln[µgZn l^{-1}] with...				
ln[Water temp (°C)]	–0.450	<0.05	Just	
Air temp (°C)	–0.619	<0.01	Very	
Rainfall (mm)	0.649	<0.001	Highly	ln[µgZn l^{-1}] = 3.42 + 0.38[mm rain]
ln[Water temp] with...				
Air temp (°C)	0.859	<0.001	Highly	ln[Water temp (°C)] = 1.98 + 0.05 [Air temp (°C)]
Rainfall (mm)	–0.466	<0.05	Just	
Wind speed (Kts)	0.478	<0.05	Just	

Figure 9·2

Dendogram illustrating the interrelationships between variables in the Avon and Heathcote River water survey. (Metal concentrations in the original data are in μg l^{-1}).



Correlation coefficients (and probabilities) describing the relationships between the monthly median concentrations of each metal in Avon and Heathcote River water sampled during July 1987–May 1988, and monthly median concentrations of that metal in the air (at aerosol sampling site 1, Chapter 7) for the same 11 months are given in Table 9·8.

The following observations can be made from Figures 9·1 and 9·2 and from the data in Tables 9·7 and 9·8 and Appendix 9·2:

The only pair of metal concentrations (μg l^{-1}) in Avon and Heathcote River water samples which are correlated are those of copper and zinc, and even this relationship is rather tenuous ($p < 0.05$) (Table 9·7 and Appendix 9·2).

None of the metals' concentrations are correlated with the pH (either positively or negatively). This is not particularly surprising, given that the overall variation in pH was minimal (total range 6.97–8.10) (Table 9·4). Thus, the finding does not detract from the potential importance of acidity in the determination of the relative proportion of a given metal present in the dissolved phase (Horowitz, 1985).

Table 9·8

Correlation coefficients (and probabilities) for the relationships between the concentrations of cadmium, copper, lead and zinc in the Avon and Heathcote Rivers ($\mu g\ l^{-1}$) and those in Christchurch air ($ng\ m^{-3}$), as determined in samples collected during the same 11 month period (July 1987–May 1988).

Pair of variables	Avon River		Heathcote River	
	Correlation coefficient (R)	Probability (p)	Correlation coefficient (R)	Probability (p)
$lnCd_{Air}$, $lnCd_{River}$	–0.506	$p > 0.1$	–0.471	$p > 0.1$
$lnCu_{Air}$, $lnCu_{River}$	–0.621	$p < 0.05$	–0.479	$p > 0.1$
$lnPb_{Air}$, $lnPb_{River}$	–0.314	$p > 0.1$	–0.269	$p > 0.1$
$lnZn_{Air}$, $lnZn_{River}$	0.226	$p > 0.1$	0.096	$p > 0.1$

More surprisingly, there are no significant positive correlations between the monthly median concentrations ($\mu g\ l^{-1}$) of each metal in Avon and Heathcote River water and those in Christchurch air ($ng\ m^{-3}$) during the same 11 month period (Table 9·8). (Most water samples were collected on one of the 5 days each month that samples of airborne particulates were being gathered.) This suggests that ambient concentrations ($ng\ m^{-3}$) of cadmium, copper, lead and zinc on a given day (as represented by airborne particulate matter) may be of only minor importance in determining the concentrations of the four metals in riverwater on that day. Possible reasons for this are as follows:

1. Dry deposition of airborne particulates (from the atmosphere, to the rivers) may be a relatively slow process.
2. Desorption of cadmium, copper, lead and zinc from airborne particulates deposited on the rivers (and liberation to the dissolved phase) may be a kinetically slow or thermodynamically unfavourable process.
3. Entry of atmospheric particulates to the rivers by direct deposition may be insignificant when compared with (longer term) runoff containing atmospherically-derived particulates which have fallen within the rivers' catchment areas. Bertine and Walawender (1978) found this second process to be relatively slow but significant in the case of the Barrett Reservoir (near San Diego); in the long term causing an estimated eightfold increase in the amount of atmospherically-derived sediment over that which could be accounted for by direct atmospheric fallout alone.
4. Dissolved cadmium, copper, lead and zinc may be significantly adsorbed onto the surfaces of atmospherically-derived particulates in the water. This might be especially true of organic-rich particulates, most prevalent in Christchurch air during the coldest months (Chapter 7).

Concentrations of dissolved cadmium in Avon and Heathcote River waters are highest in samples collected during November–February (late-spring and all summer), and lowest in samples collected during March–October (autumn to mid-spring) (Figure 9·1). Dissolved cadmium concentrations are positively correlated with the variables "water temperature", "air temperature" and "mean wind speed" (Table 9·7 and Appendix 9·2). (Predictably, "air temperature" and "water temperature" are themselves highly correlated). Possible reasons for the observed trends and correlations are as follows:

1. Transportation to the rivers of atmospherically-derived particulates which have fallen on the rivers' catchments could be a relatively slow process (Bertine and Walawender, 1978). There may be a delay of some months before the higher ambient cadmium concentrations observed in the winter months have a significant effect on the concentrations of cadmium in the rivers.
2. The proportion of cadmium adsorbed onto the suspended particulates and bottom sediments of the Avon and Heathcote Rivers may decrease as the water temperature increases. Both direct and inverse relationships have been reported to exist between the amount of cadmium adsorbed by freshwater sediments and the water temperature (Laxen, 1983).
3. Organic-rich combustion-derived airborne particulates (presumably) deposited on the rivers during the cooler months (Anon. 1986 and Chapter 7) may comprise favourable adsorption media for dissolved cadmium, and thus serve to reduce its concentration.

No clear trend is evident linking dissolved copper concentrations in the Avon and Heathcote River water samples with time (Figure 9·1). Dissolved copper concentrations in the rivers are not correlated with any of the climatological variables (Appendix 9·2), but are correlated at a "just significant" level with dissolved zinc concentrations (Table 9·7).

Dissolved lead concentrations are highest in the samples collected during July and September to January, and are lowest in samples collected during February to June and August (Figure 9·1). Apart from the high and low lead concentrations found in samples collected in July and August (respectively) the general pattern is one of high concentrations in the warmer months and low concentrations in the cooler months. There is a highly significant correlation between the dissolved lead concentrations and the variable "mean wind speed" (Table 9·7 and Appendix 9·2).

Reasons for the seasonal changes in dissolved lead concentrations could be the same as those suggested in the case of cadmium (above). (The lack of a correlation between the concentrations of dissolved cadmium and those of lead could then be due to the different responses of each metal to physico-chemical changes in its environment, such as differences in rates of transportation by runoff.)

In contrast to the trends with time shown in the cases of cadmium and lead, concentrations of dissolved zinc are lowest in samples collected during December–January

(warm months), and highest in samples gathered during June–July (cold months) (Figure 9·1). In terms of correlations, zinc concentrations are negatively related to the variables "water temperature" (just significant) and "air temperature" (very significant) (Table 9·7).

Most interesting, however, is the highly significant positive correlation between dissolved zinc concentrations and the variable "rainfall"; which may imply that runoff from galvanized-iron products during rainfall significantly increases the dissolved zinc burden of the Avon and Heathcote Rivers. It is likely that a substantial proportion of the zinc weathered from galvanized products is already in a dissolved form at the time of liberation, and is therefore readily transported. Another point worthy of consideration is that many of the drain-pipes used to mediate runoff are themselves galvanized-iron. Zinc-containing products are thus specifically used to deflect and channel rainfall, a situation which is not evident in the cases of the other three metals. The negative relationships between dissolved zinc concentrations and the variables "water temperature" and "air temperature" probably reflect the fact that more rain fell during the cooler months (Appendices 9·1 and 9·2, and Table 9·7).

Results of experiments involving the weathering of zinc from a galvanized-iron surface are presented in Chapter 13.

9·3·3 Speciations of the metals in Avon River water

The concentrations (and relative percentages) of dissolved cadmium, copper, lead and zinc in four Avon River water samples, and the amounts of each metal extracted from aliquots of the same water into n-octanol, are given in Table 9·9. Concentrations (and percentages) of cadmium in the "labile", "organic" and "inorganic" fractions of six samples of Avon River water, as determined by ASV, are given in Table 9·10.

Table 9·9

Total and n-octanol extractable concentrations of cadmium, copper, lead and zinc in four Avon River water samples (95% errors are calculated from the Student's t-distribution).

Metal	Total concn ($\mu g\ l^{-1}$)	Concn soluble in n-octanol ($\mu g\ l^{-1}$)[a]	Percent soluble in n-octanol
Cadmium			
Sample 1	0.04	0.02	50
Sample 2	0.06	0.02	33
Sample 3	0.03	0.01	33
Sample 4	0.11	0.04	36
Mean			38
Std deviation			8
95% error on mean			±10

Table 9·9 continued...

Metal	Total concn ($\mu g\ l^{-1}$)	Concn soluble in n-octanol ($\mu g\ l^{-1}$)[a]	Percent soluble in n-octanol
Copper			
Sample 1	1.5	0.6	40
Sample 2	0.8	0.2	25
Sample 3	1.7	1.0	60
Sample 4	1.8	1.2	67
Mean			48
Std deviation			19
95% error on mean			±24
Lead			
Sample 1	0.5	0.2	40
Sample 2	0.7	0.2	29
Sample 3	0.5	0.2	40
Sample 4	0.3	0.1	33
Mean			36
Std deviation			5
95% error on mean			±6
Zinc			
Sample 1	39	5	13
Sample 2	39	8	21
Sample 3	26	10	38
Sample 4	34	7	21
Mean			23
Std deviation			11
95% error on mean			±14

Notes: a. Microgram per litre of water.

Table 9·10

Concentrations and percentages of cadmium in the "labile", "organically bound" and "inorganically bound" fractions of six samples of Avon River water, as determined by ASV.

	Labile	Organically bound	Inorganically bound	Total
Concentrations ($\mu gCd\ l^{-1}$)				
Sample 1	0.07	0.02	0.01	0.10
Sample 2	0.08	0.03	0.01	0.12
Sample 3	0.09	0.03	0.01	0.13
Sample 4	0.12	0.04	0.02	0.18
Sample 5	0.06	0.01	0.01	0.08
Sample 6	0.08	0.02	0.01	0.11

Table 9·10 continued...

	Labile	Organically bound	Inorganically bound	Total
Percent of total cadmium				
Sample 1	70	20	10	100
Sample 2	67	25	8	100
Sample 3	69	23	8	100
Sample 4	67	22	11	100
Sample 5	75	13	13	101[a]
Sample 6	73	18	9	100
Mean	70	20	10	
Standard devn	3	4	2	
95% error[b]	±3	±4	±2	

Notes: **a.** Rounding error.
b. Student's t-distribution.

Of the total amount of each metal in the dissolved fraction of the Avon River water samples, the "lipid-soluble" (n-octanol extractable) portion comprises 38% of the cadmium, 48% of the copper, 36% of the lead and 23% of the zinc (Table 9·9).

Assuming that these results are true in the general case (*i.e.* along most of the Avon River and during most of the year) , it could be expected that about 40% of the cadmium in the dissolved fraction of Avon River water would experience little or no resistance in traversing a biomembrane. It is thought that the lipid-soluble fraction of a metal predominantly represents metal species which are complexed with or bound to various hydrophobic ligands (Florence, 1988).

The high mean amount of n-octanol-extractable copper (48%) is likely to reflect copper's typically strong association with organic ligands (Florence, 1982).

Coefficients of variation on the mean amounts of "lipid-soluble" cadmium, copper, lead and zinc are 21%, 48%, 14%, and 40% (respectively). These figures represent the combination of random analytical variations with differences between sites in the proportion of each metal which is soluble in n-octanol.

Most (70%) of the cadmium in the six Avon River water samples that were analysed by ASV was present in an ASV-labile form (Table 9·10). This fraction represents both free (aquocomplexed) Cd^{2+}, and species which are quickly dissociated by application of an electrical potential.

Because the ASV-lability of a metallic-species is a measure of that species' kinetic stability under the parameters imposed by experimental conditions (such as the time-scale and the pH), a species' ASV-lability bears little relation to its thermodynamic stability under equilibrium conditions in freshwaters (Skogerboe *et al.* 1980). However, the size of the

ASV-labile fraction of a metal (measured under the conditions used in this study) has been reported to correlate reasonably well with toxicity of that metal to aquatic organisms (Florence, 1988).

Measured by ASV, cadmium bound to organic and inorganic material was found to represent 20% and 10% (respectively) of total cadmium in the <0.025 μm fraction of the six Avon River water samples (Table 9·10).

9·4 Conclusion

The geometric mean concentrations of cadmium, copper, lead and zinc in samples of Avon and Heathcote River water collected over 12 months are 0.14, 1.9, 2.5 and 39 $\mu g\ l^{-1}$, respectively.

The geometric mean concentrations of dissolved cadmium, copper, and zinc in Avon and Heathcote River water samples are all higher than levels reported to be typical of the world's unpolluted freshwaters, but lower than concentrations often found in rivers in industrialized areas. Geometric mean lead concentrations in Avon and Heathcote River water samples are within the ranges quoted for the world's unpolluted freshwaters.

However, relative to New Zealand riverwater background concentrations of cadmium, copper, lead and zinc, levels of the four metals in Avon and Heathcote River water samples are substantially enriched. Enrichments factors (relative to background levels) follow the order zinc (260) > lead (83) > cadmium (14) > copper (13).

Despite the higher degree of industrialization associated with the Heathcote River in the past, there are no significant differences between concentrations of dissolved cadmium, copper, lead or zinc concentrations in Heathcote River water samples and those in Avon River water samples.

Concentrations of dissolved cadmium, copper, lead and zinc are not positively correlated with the concentrations of the metals in the air over the same 11 month period, suggesting that the atmospheric levels of each metal on a given day are of only minor importance in determining dissolved metal concentrations in riverwater *on that day*. (However, fallout of airborne particulates onto the rivers' catchment areas and subsequent transportation of these particulates to the rivers could result in a time delay effect.)

Dissolved lead and cadmium concentrations are generally highest in samples collected during the warmest months, and lowest in samples collected during the coolest months, dissolved copper levels showed no clear trend with time, and dissolved zinc concentrations are generally highest in samples collected during the coolest months and lowest in samples collected during the warmest months.

Runoff from the weathering of galvanized-iron products is likely to be responsible for a large part of the variation in dissolved zinc concentrations with time, for three reasons:

1. Zinc concentrations are highly (and positively) correlated with rainfall, and most rain fell during the coolest months. (Rainfall was negatively correlated with water temperature.)

2. The extremely high enrichment factor for zinc compared with background levels suggests that a source of the metal exists which emits zinc more or less uniquely.
3. Many galvanized-iron products are specifically used to deflect and channel rainfall.

Possible reasons for the trends shown by dissolved cadmium and lead concentrations with time are more speculative in nature, and include the (possible) time-delay effect between the deposition onto the rivers' catchment areas of airborne particulates and their transportation to the rivers, temperature-related sorption effects, and the potential for organic-rich airborne particulates (likely to fall on the rivers in the cooler months) to adsorb dissolved metals. Dissolved cadmium concentrations are positively correlated with the climatological variables "water temperature" and "mean wind speed", whereas dissolved lead concentrations are positively correlated with "mean wind speed" only.

About 40% of the cadmium in four samples of Avon River water was soluble in n-octanol. Cadmium in this fraction would be expected to be capable of crossing a biomembrane with relative ease. "Labile", "organically bound" and "inorganically bound" cadmium (as detected by ASV) comprised 70%, 20% and 10% of the total cadmium in the <0.025 μm fraction of six further samples of Avon River water.

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9·6 Appendices

Appendix 9·1 (section 9·3·1)

Means, standard deviations, and medians of the concentrations of cadmium, copper, lead, zinc and the parameter pH in Avon and Heathcote River water over 12 months, and values of the water temperature and meteorological parameters relating to the sampling days. Note: each mean or median is that of water sampled from six sites along each River. Confidence errors (95%) on the means are in all cases ±0.90[std deviation].

Variable	Month and year					
	July 1987	Aug	Sept	Oct	Nov	Dec 1987
Avon River						
Metal concns ($\mu g\ l^{-1}$)						
Cadmium						
Arithmetic mean	0.08	0.09	3.51[a]	0.07	0.22	0.17
Standard deviation	0.03	0.05	4.21	0.02	0.12	0.10
Median	0.09	0.08	2.09	0.07	0.24	0.17
Copper						
Arithmetic mean	3.1	2.3	2.6	3.9	3.4	0.6
Standard deviation	2.1	1.7	1.6	2.6	1.9	0.2
Median	3.0	1.6	2.0	4.0	2.9	0.7
Lead						
Arithmetic mean	8.6	<0.4	4.5	7.9	5.4	7.0
Standard deviation	1.4		2.6	4.4	2.6	2.3
Median	9.6	<0.4	5.1	6.7	4.3	6.6
Zinc						
Arithmetic mean	74	23	32	26	27	18
Standard deviation	41	5	18	9	12	14
Median	72	24	27	24	31	13
Other parameters						
pH						
Arithmetic mean	7.49	7.45	7.65	7.33	7.53	7.88
Standard deviation	0.12	0.10	0.31	0.27	0.14	0.44
Median	7.50	7.45	7.63	7.33	7.59	7.83
Water temp (°C)	10	10	14	17	17	19
Air temp (°C)	8	13	12	19	17	21
Rainfall (mm)	4.1	0	0.4	0	0	0
Mn wind spd (Kts)	11	5	6	5	12	10

Appendix 9·1 continued...

Variable	Month and year					
	Jan 1988	Feb	Mar	Apr	May	Jun 1988
Avon River						
Metal concns ($\mu g\ l^{-1}$)						
Cadmium						
Arithmetic mean	0.27	0.44	0.13	0.13	0.12	0.06
Standard deviation	0.15	0.20	0.01	0.01	0.05	0.02
Median	0.29	0.39	0.13	0.13	0.12	0.06
Copper						
Arithmetic mean	1.4	1.7	1.9	1.2	0.8	1.9
Standard deviation	0.5	0.4	1.1	0.6	0.4	0.7
Median	1.4	1.7	1.7	0.8	0.7	1.7
Lead						
Arithmetic mean	12.5	1.3	1.0	0.8	1.1	1.9
Standard deviation	3.5	0.4	0.3	0.1	0.1	0.4
Median	12.6	1.2	0.9	0.8	1.1	2.2
Zinc						
Arithmetic mean	16	65	24	40	37	110
Standard deviation	11	65	13	16	23	100
Median	16	44	20	42	28	80
Other parameters						
pH						
Arithmetic mean	7.16	7.19	7.18	7.70	7.39	7.09
Standard deviation	0.20	0.18	0.22	0.17	0.13	0.21
Median	7.15	7.23	7.20	7.64	7.34	6.97
Water temp (°C)	19.5	19	15	15	9	10
Air temp (°C)	20	18	15	10	9	5
Rainfall (mm)	0	0	1.1	0.2	0	1.6
Mn wind spd (Kts)	10	7	7	7	2	6

Appendix 9·1 continued...

Variable	Month and year					
	July 1987	Aug	Sept	Oct	Nov	Dec 1987
Heathcote River						
Metal concns ($\mu g\ l^{-1}$)						
Cadmium						
Arithmetic mean	0.18	0.10	1.15[a]	0.09	0.25	0.20
Standard deviation	0.07	0.04	0.57	0.04	0.13	0.08
Median	0.19	0.09	0.95	0.82	0.23	0.18
Copper						
Arithmetic mean	4.4	15.6	2.1	3.5	4.8	0.8
Standard deviation	1.8	8.1	1.0	2.3	0.8	1.0
Median	4.9	14.8	1.8	2.7	4.6	0.6
Lead						
Arithmetic mean	6.0	<0.4	6.6	4.2	2.8	11.5
Standard deviation	2.5		2.9	1.5	2.4	3.3
Median	8.0	<0.4	6.0	4.2	3.0	10.6
Zinc						
Arithmetic mean	310	69	54	45	44	27
Standard deviation	80	23	7	19	27	27
Median	320	67	55	45	39	15
Other parameters						
pH						
Arithmetic mean	7.49	7.55	7.71	7.56	7.77	8.05
Standard deviation	0.30	0.27	0.33	0.26	0.23	0.30
Median	7.50	7.48	7.73	7.52	7.72	8.10
Water temp (°C)	10	10	14	17	19	16
Air temp (°C)	8	13	12	19	17	21
Rainfall (mm)	4.1	0	0.4	0	0	0
Mn wind spd (Kts)	11	5	6	5	17	21

Appendix 9·1 continued...

Variable	Month and year					
	Jan 1988	Feb	Mar	Apr	May	Jun 1988
Heathcote River						
Metal concns ($\mu g\ l^{-1}$)						
Cadmium						
Arithmetic mean	0.28	0.55	0.16	0.14	0.11	0.09
Standard deviation	0.25	0.21	0.02	0.02	0.05	0.04
Median	0.25	0.51	0.17	0.14	0.09	0.08
Copper						
Arithmetic mean	2.1	2.4	3.1	0.9	0.9	1.6
Standard deviation	0.8	1.1	2.8	0.4	0.3	0.5
Median	2.3	2.4	2.1	0.7	0.9	1.5
Lead						
Arithmetic mean	12.1	1.3	1.3	0.9	1.1	1.6
Standard deviation	1.9	0.9	0.3	0.1	0.8	0.5
Median	12.4	1.0	1.1	1.0	1.0	1.9
Zinc						
Arithmetic mean	29	90	62	70	53	91
Standard deviation	15	83	63	31	44	57
Median	30	60	27	74	28	80
Other parameters						
pH						
Arithmetic mean	7.40	7.76	7.78	7.79	7.41	7.18
Standard deviation	0.18	0.20	0.21	0.14	0.18	0.10
Median	7.39	7.82	7.78	7.72	7.30	7.13
Water temp (°C)	19	18	15	14	9	10
Air temp (°C)	20	18	15	10	9	5
Rainfall (mm)	10	7	7	7	2	6
Mn wind spd (Kts)	10	7	7	7	2	6

Note: a. Identified as an outlier.

Appendix 9·2 (section 9·3·2)

Correlation matrix for the variables in the Avon and Heathcote River water survey. Number of pairs = 24. Pearson's probabilities are as follows: R>0.630, p<0.001; R>0.517, p<0.01; R>0.492, p<0.02; R>0.406, p<0.05

	ln[µg l^{-1} Cd]	ln[µg l^{-1} Cu]	ln[µg l^{-1} Pb]	ln[µg l^{-1} Zn]	pH	ln[°C water]	[°C air]	Rain fall (mm)	Mean wind spd (Kts)
lnCd	1								
lnCu	–0.023	1							
lnPb	0.118	–0.008	1						
lnZn	–0.066	0.432	–0.079	1					
pH	0.253	–0.119	0.125	–0.153	1				
ln[°C water]	0.625	–0.039	0.366	–0.450	0.328	1			
°C air	0.541	0.036	0.332	–0.619	0.379	0.859	1		
Rain	–0.177	0.247	0.250	0.649	–0.174	–0.466	–0.558	1	
Wnd spd	0.534	0.180	0.583	0.062	0.327	0.478	0.350	0.308	1

CHAPTER 10
ADSORPTION OF CADMIUM BY A CHRISTCHURCH SOIL

10·1 Introduction

10·1·1 Overview and aims

Sorption is the primary factor governing the mobility of metal ions in soils, and encompasses three processes: adsorption, absorption and precipitation (Puls and Bohn, 1988; Chubin and Street, 1981). Because of the usual dominance of the first process in metal ion immobilization by soils, the terms *sorption* and *adsorption* are often used synonymously. Unless otherwise stated (and in keeping with usual practice), the term *adsorption* will be taken to represent all sorption processes throughout this chapter.

The amount of cadmium deposited yearly on the land has increased markedly over the last century, due both to a general increase in atmospheric cadmium levels, and to the repeated application to farmland of phosphatic-fertilizers and sewage sludges (sections 1·3·1 and 2·1·2e; Jones and Symon, 1987; Rothbaum *et al.* 1986). Cadmium deposited on the soil surface can either accumulate in the topsoil (by sorption processes), or leach through the soil to the ground water (Emmerich *et al.* 1982). Unfortunately, both of these processes comprise potential health hazards; cadmium associated with topsoil may be taken up in food crops, and that in ground water may eventually enter the water supply (Symeonides and McRae, 1977; Christensen, 1985).

Three important soil components in terms of cadmium adsorption are clay minerals, organic matter, and iron and manganese oxides (Haas and Horowitz, 1986; Laxen, 1983; Wold and Pickering, 1981). Of these, trace elements adsorbed on clay minerals are (in general) easily mobilized by plants (Kabata-Pendias and Pendias, 1985). Cadmium dissolved in interstitial soil water (rather than adsorbed) is also easily available to plants (Khalid, 1980).

Factors which have been reported to influence cadmium adsorption by soils or soil components from solution are numerous, and are listed in Table 10·1.

Although worldwide there has been a substantial amount of research relating to cadmium adsorption processes in soils (Table 10·1) few such studies have been conducted on New Zealand soils (section 2·1·2e). (The adsorption characteristics of soils vary from country to country.)

The aim of this study was to examine cadmium adsorption by a Christchurch soil (Tai Tapu silt loam) at cadmium concentrations typical of those found in the environment. This involved:

1. studies of cadmium adsorption by individual soil components and by whole soil;
2. studies on the effects of pH changes on cadmium adsorption by whole soil;
3. studies in the competitive adsorption of cadmium and lead, and cadmium and zinc, onto whole soil.

Table 10·1

Factors which influence the amount of cadmium adsorbed by soils or soil components from solution.

Factor	Comments	References
Adsorption density	Amount adsorbed decreases as adsorption density increases	Garcia-Miragaya *et al.* 1986 Laxen, 1983 Navrot *et al.* 1978
Competing cations, exchangeable cations, and cation exchange capacity	Effect of competing cations often only marginal, as different metal ions show different affinities for particular adsorption sites	Abd-Elfattah and Wada, 1981 Christensen, 1984a Elliot *et al.* 1986 Farrah and Pickering, 1977 Garcia-Miragaya and Page, 1977 Haghiri, 1976 O'Connor *et al.* 1984 Ramamoorthy and Rust, 1978 Sadiq and Zaidi, 1981
Concn of Cd^{2+}	Isotherms at low Cd^{2+} concns differ from those at high Cd^{2+} concns	Christensen, 1984a and 1984b Reid and M^{c}Duffie, 1981
E_h and pH	Cd^{2+} exists at positive E_h values and at pH values of less than 8 Adsorption decreases as pH decreases Under reducing conditions, formation of CdS may reduce adsorption	Christensen, 1984a Elliot *et al.* 1986 Farrah and Pickering, 1977 Gerritse and Van Driel, 1984 Hahne and Kroontje, 1973 Hermann and Neumann-Mahlkau, 1985 Reid and M^{c}Duffie, 1981 Trefry and Metz, 1984
Ionic strength	Adsorption generally decreases as ionic strength increases Higher ionic strengths alter the properties of the electric double-layer, increase metal ion activities, and provide competing cations and possible complexing ligands	Elliot, 1983 Garcia-Miragaya and Page, 1976 Gerritse and Van Driel, 1984 O'Connor *et al.* 1984 Wold and Pickering, 1981
Ligand complexation	Both positive and negative effects, depending on the ligand	Chubin and Street, 1981 Farrah and Pickering, 1977 and 1978 Garcia-Miragaya and Page, 1976 Hahne and Kroontje, 1973

Table 10·1 continued...

Factor	Comments	References
Nature of the adsorptive surface	Important sorptive substrates include clay minerals, organic matter, and iron and manganese oxides	Brown *et al.* 1983 Emmerich *et al.* 1982 Eriksson, 1988 Farrah and Pickering, 1977 Garcia-Miragaya and Page, 1978 Gerritse and Van Driel, 1984 Haas and Horowitz, 1986 Navrot *et al.* 1978 Neal and Sposito, 1986 Petruzzelli *et al.* 1978 Puls and Bohn, 1988 Ram and Verloo, 1985
Temperature	Both direct and inverse relationships reported	Laxen, 1983
Time	Attainment of equilibrium can take several days in some cases Leaving the soil to age can effect reversibility	Aringhieri *et al.* 1985 Christensen, 1984a and 1984b Eriksson, 1988 Laxen, 1983 Sidle and Kardos, 1977

10·1·2 Definition of terms

Throughout this chapter, terms relating to adsorption will be in accordance with definitions given by Laxen (1983). Under this scheme, adsorption of a metal is represented as a surface complexation process:

$$S + Me \rightleftharpoons SMe \qquad (1),$$

where S is the sorptive surface and Me is the metal ion (charges are omitted). The *equilibrium constant* for this process (K_{eq}) is defined as:

$$K_{eq} = a_{SMe} / a_S \times a_{Me} \qquad (2),$$

where a_i represents the activity of species i. For the purposes of experiment, K_{eq} can be approximated by a *conditional equilibrium constant*, K*:

$$K^* = [SMe] / [Solid_T] \times [Me_{Diss}] \qquad (3)$$

where [SMe] is the concentration of adsorbed metal (usually given in $\mu g\ l^{-1}$), $[Me_{Diss}]$ is the dissolved metal concentration (usually given in $\mu g\ l^{-1}$), and $[Solid_T]$ is the total solids concentration (usually given in $mg\ l^{-1}$). The conditional equilibrium constant (which will be expressed in units of $ml\ g^{-1}$ throughout this chapter) is conditional because it is influenced by all the factors listed in Table 10·1.

The *percent adsorption* is defined as follows:

$$\% \text{ Adsn} = 100 \text{ x } \{[\text{SMe}] / ([\text{Me}_{\text{Diss}}] + [\text{SMe}])\} \quad (4)$$

This expression can be rearranged to provide the ratio $[\text{SMe}] / [\text{Me}_{\text{Diss}}]$ required for equation 3:

$$[\text{SMe}] / [\text{Me}_{\text{Diss}}] = \% \text{ Adsn} / (100 - \% \text{ Adsn}) \quad (5)$$

The *adsorption density* (Γ_{Me}), usually expressed in $\mu g\ g^{-1}$, is defined as follows:

$$\Gamma_{\text{Me}} = [\text{SMe}] / [\text{Solid}_{\text{T}}] \quad (6).$$

The adsorption isotherms of metal ions on soils are often best described by one of two models. The first of these is the *Langmuir* adsorption model, which is represented by the following (linearized) equation:

$$[\text{Me}_{\text{Diss}}] / \Gamma_{\text{Me}} = 1/b\ [\text{Me}_{\text{Diss}}] + 1/kb \quad (7)$$

where b and k are constants (Navrot *et al.* 1978). Assumptions implicit in the Langmuir adsorption model include (a) the independence and equivalence of adsorption sites (so that adsorption enthalpy is not influenced by surface coverage), (b) reversible equilibrium to monolayer coverage and (c) fixed site adsorption and immobility of adsorbate (Atkins, 1983; Navrot *et al.* 1978). The second adsorption model, that of *Freundlich*, is described by the following (linearized) equation:

$$\ln \Gamma_{\text{Me}} = 1/b \ln [\text{Me}_{\text{Diss}}] + 1/kb \quad (8)$$

(where b and k are constants) (O'Connor *et al.* 1984). The Freundlich model is empirical in nature, and takes into account the fact that adsorption enthalpy often declines markedly as surface coverage increases, an effect which indicates non-uniformity of the substrate's adsorption sites (Atkins, 1983; Moore, 1974).

In Langmuir-type adsorption, the amount adsorbed approaches a finite limit as the concentration of the species being adsorbed is increased; whereas under the Freundlich adsorption model, no theoretical adsorption limit exists (Moore, 1974).

10·2 Method

10·2·1 Isolation and characterization of soil components

A large sample (about 10 kg) of Tai Tapu silt loam was collected from a field in the Christchurch suburb of Halswell, oven dried (at 95 °C for several days), lightly crushed, sieved at 563 μm (with coarser particles being discarded) and homogenized. Tai Tapu silt loam was chosen because it is commonly found throughout the Christchurch area (Raeside

and Rennie, 1974). Under the Soil Taxonomy system, Tai Tapu silt loam is classified as an *aquent* soil (Anon. 1985).

A portion of this sample was separated into three size fractions, the designations of which under the Wentworth classification system were "clay" (< 3.9 μm), "silt" (3.9–63 μm) and "very fine to medium sand" (63–563 μm) (Lewis, 1981). This was achieved by the following method:

1. A 200 g sample of the Tai Tapu silt loam was sieved at 63 μm (with a nylon sieve). Material coarser than this size comprised the "very fine to medium sand" fraction (which will be referred to hereafter simply as the "sand" fraction).
2. Material finer than 63 μm was divided into 20 g sub-samples. Each of these was added to a solution containing 50 ml of 10% (by weight) AR sodium carbonate (as a dispersing agent) and 950 ml of double-distilled water in a clean 1 000 ml measuring cylinder. The solutions were stirred thoroughly and left to stand for four hours, after which time the top 600 ml was drawn off with an U-shaped siphon. Clay (<3.9 μm) in this solution was flocculated with 40 ml of saturated AR sodium chloride solution, collected, washed thoroughly with double-distilled water by centrifugation until dispersal had started, and oven-dried. Solutions remaining in the measuring cylinders were made up to 1 000 ml with double-distilled water, and the clay-collection process was repeated, seven times (in order to collect all the clay).
3. Material remaining at the bottom of each cylinder after the final clay collection step is predominantly silt (3.9–63 μm) (Lewis, 1981). The silt fraction was collected, washed several times with double-distilled water and separated using a centrifuge, and oven-dried.

The three size fractions of the Tai Tapu silt loam were analysed by X-ray powder diffraction (XRPD) using the method given in section 5·2. Diffraction peaks were found to correspond with those of trioctahedral illite, quartz and low-albite in the clay fraction, and with quartz and low-albite (only) in the silt and sand fractions. *Illite* is the name given to a group of (generally non-swelling) clay-grade micas; it is an alumino-iron-silicate mineral of general composition 38–54% SiO_2, 8–29% Al_2O_3 and 2–23% Fe_2O_3 and FeO (Brindley and Brown, 1980; Reid and McDuffie, 1981). *Low-albite* is a feldspar (Brindley and Brown, 1980). D-values and relative intensities of the diffraction peaks from each of the three samples and those given in the literature for illite, quartz and low-albite are given in Appendix 10·1. Glyceration of the <3 μm size fraction produced no shifts in the positions of that sample's diffraction peaks, implying that the clay was of a non-expanding type; this was regarded as further evidence that the clay was likely to be (predominantly) illite (Brindley and Brown, 1980).

The organic content, and the concentrations of cadmium, lead and zinc in the clay and silt fractions and the whole soil were determined using the methods given in sections 3·2·1 and 3·2·2 (respectively). Values of these parameters are listed in Appendix 10·2. The pH of an equilibrated solution comprising 10 g of Tai Tapu silt loam and 10 ml of double-distilled water was found to be 5.70 (using a pH-meter) and the oxidation potential of the same

solution was found to be 0.140 V (using an E_h-meter with a saturated calomel electrode). The pH of Tai Tapu silt loam has been previously reported to range from 5.0 to 7.0 (Anon. 1968).

Organic matter was removed from a sample of the processed Tai Tapu silt loam by oxidation with 5% hydrogen peroxide for 24 hr at 25 °C at pH 5.8 (500 ml of hydrogen peroxide per gram of soil) (Jackson, 1958).

Amorphous coatings and crystals of free iron and manganese oxides were removed from another sample of the processed Tai Tapu silt loam by the method of Mehra and Jackson (1960). To each gram of the soil was added 40 ml of 0.3 M AR sodium citrate solution and 5 ml of 1 M AR sodium bicarbonate solution; the mixture was brought to 80 °C in a water-bath, and after addition of 1 g of solid AR sodium dithionite ($Na_2S_2O_4$), was stirred constantly for 1 minute and occasionally for 15 minutes. Saturated AR sodium chloride solution (10 ml) was used to flocculate the soil, which was then washed thoroughly with double-distilled water (with the use of a centrifuge) and oven-dried.

Silica sand, used for one of the experiments, had been collected previously from a New Zealand beach, acid washed, double-distilled water rinsed, and dried.

10·2·2 Methodology of the adsorption experiments

Adsorption experiments were conducted by the *batch-equlibration* technique. Accurately weighed (0.5000 ± 0.0060) g samples of each substrate were placed in 250 ml conical flasks. Conical flasks had previously been acid-washed, rinsed thoroughly with double-distilled water, and oven-dried.

Solutions with cadmium concentrations ranging from 0.010 to 0.230 μg ml^{-1} were prepared in 0.01 M AR sodium acetate/acetic acid buffers. In the competitive adsorption experiments, these solutions also contained either zinc (40 μg ml^{-1}), or lead (3 μg ml^{-1}). The pH values of the buffer solutions were 5.70 (the pH of the soil solution), 7.0 and 8.0. Under these conditions, it would be expected that almost all of the cadmium in solution would be present in the "free" (aquocomplexed) ionic form (Cd^{2+}) (Hermann and Neumann-Mahlkau, 1985). The proportion of 0.01 M acetic acid to 0.01 M sodium acetate required for each pH was calculated using the formula:

$$pH = pK_a - \log_{10} (\text{moles } X^- / \text{moles HX}),$$

(where the pK_a of acetic acid is 4.74). The buffer solution's pH was then checked using a pH-meter.

The regulation of pH by the buffers was considered to be of greater importance than possible perturbations in soil adsorption characteristics which may have resulted from buffer use (Table 10·1). The low concentration of the buffer solutions (0.01 M) would tend to minimize competitive adsorption of cadmium by sodium ions and possible cadmium complexation effects by acetate anions. Wold and Pickering (1981) reported that significant

competition to metal ion adsorption by sodium ions occurs only at sodium ion concentrations of above 0.1 M.

The comparatively low solution cadmium concentrations used in this study were similar to those used by other researchers when investigating cadmium adsorption phenomena under conditions approximating those found in the environment (Christensen, 1984; Garcia-Miragaya and Page, 1976 and 1977; Garcia *et al.* 1984; O'Connor *et al.* 1984).

To each conical flask (containing about 5 g of substrate) was added 35 ml of the appropriate solution (thus, the total solids concentration ([$Solid_T$]) was in all cases about 14 300 mg l^{-1}). Conical flasks were then covered, left in a water bath at 25 °C for 48 hr, and occasionally agitated. After 48 hr, the solutions were centrifuged at 5 000 r.p.m. for 5 minutes.

The concentration of cadmium in the equilibrium supernatant solutions was determined by GFAAS, using the parameters given in section 3·2·2. Atomic absorption peaks for cadmium were sharp and symmetrical. In the case of the competitive adsorption experiments, lead and zinc in the supernatant solutions were analysed by FAAS, using the parameters given in Chapter 14. Standards and blanks for each analysis were prepared in 0.01 M acetic acid/sodium acetate buffers of the same acidities as those used in experiments. The method of standard additions revealed that no significant (>4%) interferences were present in the GFAAS analysis of cadmium, or in the FAAS analyses of lead and zinc.

The 48 hr "optimum equilibration time" was estimated by addition of 35 ml of 0.1 μgCd ml^{-1} solution (buffered at pH 5.70) to seven conical flasks, each of which contained (0.5000 g ± 0.0060 g) samples of the clay (<3.9 μm) fraction of Tai Tapu silt loam. Equilibrium solutions were analysed for cadmium (by GFAAS) after being left in the water bath at 25 °C for 3.5 min, 20 min, 1 hr, 3 hr, 6.5 hr, 24 hr and 123 hr. The results of this experiment are presented in section 10·3·1.

In most cases, experiments were carried out in duplicate. In order to assess whether or not any cadmium was being adsorbed on the inner walls of the conical flasks (Chen and Zhang, 1984), cadmium-containing solutions were placed in 12 clean conical flasks and left at 25 °C for 48 hr. However, no statistically significant reduction of cadmium concentrations in the solutions was detected (using GFAAS) after this time.

10·3 Results and discussion

10·3·1 Determination of the optimum equilibration time

The results of the experiment designed to measure the effect of time on the adsorption of cadmium by the clay fraction (<3.9 μm) of Tai Tapu silt loam (at 25 °C and pH 5.70) are given in Table 10·2. The data from Table 10·2 relating to the percent adsorption of cadmium after various equilibration times is illustrated in Figure 10·1.

Table 10·2

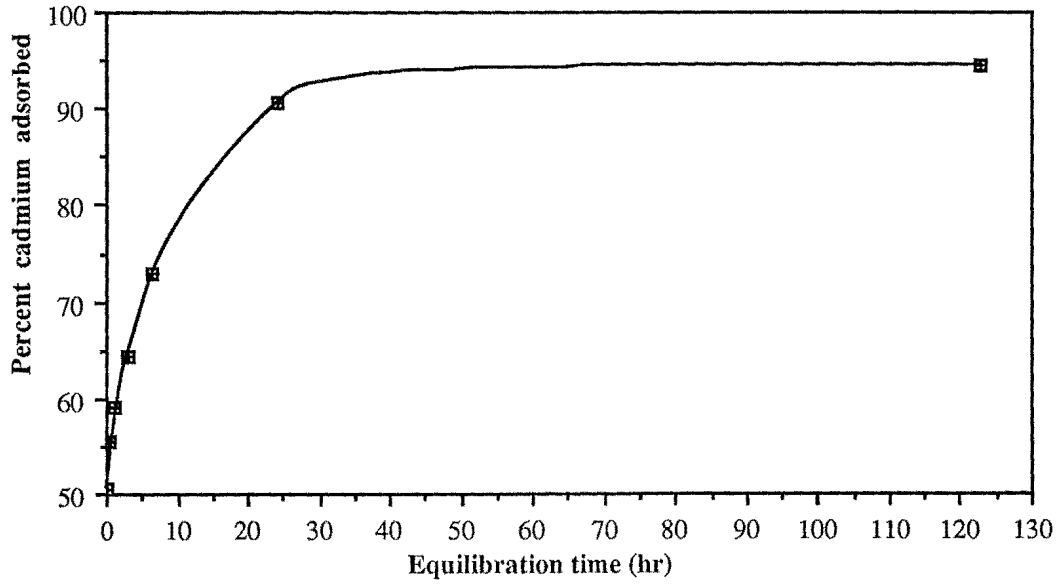
Effect of equilibration time on the amount of cadmium adsorbed by the clay fraction of Tai Tapu silt loam at 25 °C and a pH of 5.70.

Equilibration time (hr)	Observed adsorption density (Γ_{Cd}) (μgCd g(clay)$^{-1}$)	Highest possible adsorpn density (Γ_{Max}) (μgCd g(clay)$^{-1}$)	% Adsn	% Adsn rate[a] (%Ads hr^{-1})
0.058	3.50	6.92	50.6	867
0.33	3.87	6.98	55.4	17.5
1	4.12	6.96	59.1	5.6
3	4.51	6.99	64.5	2.7
6.5	5.12	7.02	72.9	2.4
24	6.27	6.92	90.6	1.0
123	6.58	7.00	94.6	0.04

Note: a. % Adsn rate calculated as Δ (%Adsn) / Δ time.

Figure 10·1

The relationship between equilibration time and the percent of cadmium adsorbed by the clay fraction of Tai Tapu silt loam at 25 °C and pH 5.70.



The following observations can be made from Figure 10·1 and the data in Table 10·2:

1. The rate of cadmium adsorption by the clay was initially extremely high, and decreased with time in an approximately exponential manner ($p<0.01$). The equation of the relationship is: %Adsn rate $= 839 \times 10^{-\text{Time(hr)}} - 44.6$. The high initial cadmium adsorption rate could be due to the existence of highly specific cadmium adsorption sites on the clay; this topic is discussed in further detail in section 10·3·2.
2. About 95% of the cadmium in solution was adsorbed by the clay after an equilibration period of 123 hr. However, of the total amount of cadmium adsorbed by the clay in

123 hr, over half (53%) was adsorbed within the first 3.5 minutes, and most (95.8%) was adsorbed within the first 24 hr. By interpolation, it was estimated that almost all (>99%) of the cadmium adsorbed by the clay in 123 hr was likely to have been adsorbed within 48 hours.

Because of these results, an equilibration period of 48 hr was used in the remaining cadmium adsorption experiments. (In subsequent discussion, the cadmium concentrations in solutions left for 48 hr will be referred to as "equilibrium" concentrations.)

Equilibration times used by other researchers when examining cadmium adsorption by soils and clays range from 1 hr (Garcia-Miragaya and Page, 1976, 1977 and 1978; O'Connor *et al.* 1984) to 50 days (Sadiq and Zaidi, 1981). Overall, however, the most commonly used equilibration time appears to be 24 hr (Aringhieri *et al.* 1985; Elliot *et al.* 1986; Haas and Horowitz, 1986; Farrah and Pickering, 1977 and 1978; Navrot *et al.* 1978; Reid and McDuffie, 1981; Wold and Pickering, 1981).

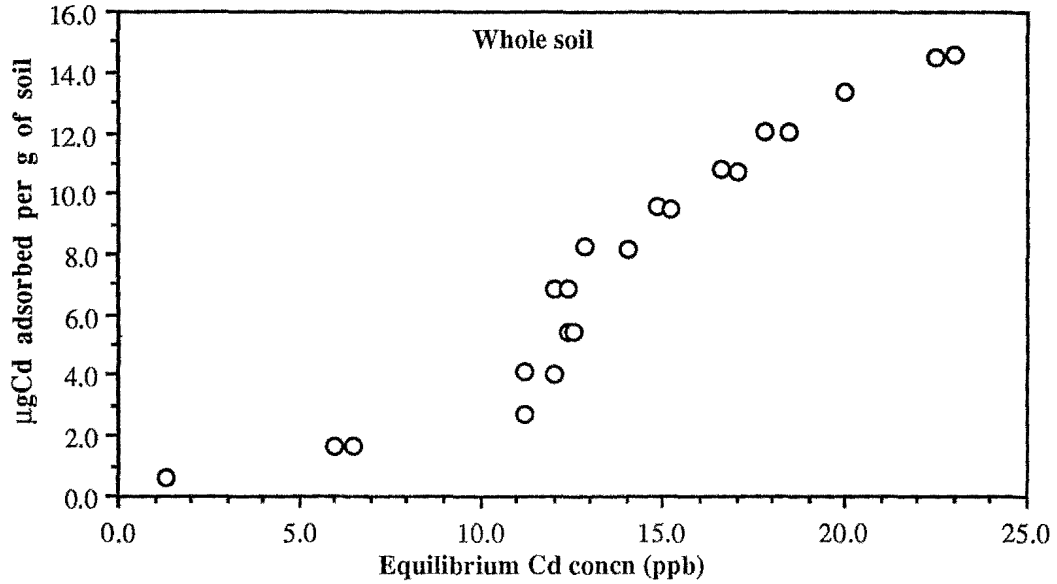
10·3·2 Adsorption of cadmium by Tai Tapu silt loam and its components

All experiments relating to the adsorption of cadmium by whole soil and individual soil components were conducted at a pH of 5.70 (the pH of the soil solution), an ionic strength (caused by the buffer) of 0.01, a temperature of 25 °C, and a total solids concentration of (14.3 ± 0.2) g l^{-1}. The full data sets describing cadmium adsorption by Tai Tapu silt loam, the three size fractions separated from it (sand, silt and clay), silica sand, Tai Tapu silt loam with organic matter removed, and Tai Tapu silt loam with iron and manganese oxides removed are given in Appendices 10·3–10·9. Statistics summarizing the percentage of cadmium adsorbed by, and the conditional equilibrium constants (K*) for cadmium adsorption by, Tai Tapu silt loam, its components and silica sand are given in Table 10·3. Simple adsorption isotherms (*i.e.* plots of the equilibrium cadmium concentration versus the adsorption density), derived from the data in Appendices 10·3–10·9, are presented in Figure 10·2.

About nine-tenths (87.3%) of the available cadmium was adsorbed by the (whole) Tai Tapu silt loam, implying that at its natural pH, the soil has a high affinity for trace amounts of cadmium, and suggesting that the mobility of cadmium in Tai Tapu silt loam would be limited (Garcia-Miragaya and Page, 1977) (Table 10·3). The conditional equilibrium constant (K*) for cadmium adsorption by the whole soil under the conditions described is (528 ± 53) ml g^{-1}. The equilibrium constant for cadmium adsorption by Tai Tapu silt loam under environmental conditions would probably be higher than this figure, as the ionic strength of the soil solution would normally be less than 0.01 (section 10·1·1).

Figure 10·2

Cadmium adsorption by Tai Tapu silt loam, components separated from Tai Tapu silt loam, and silica sand at 25 °C, pH 5.70, ionic strength 0.01, and total solids concentration (14.3 ± 0.2)g l^{-1}. Initial cadmium concentrations in solution ranged from 10.0–230 μg l^{-1}.



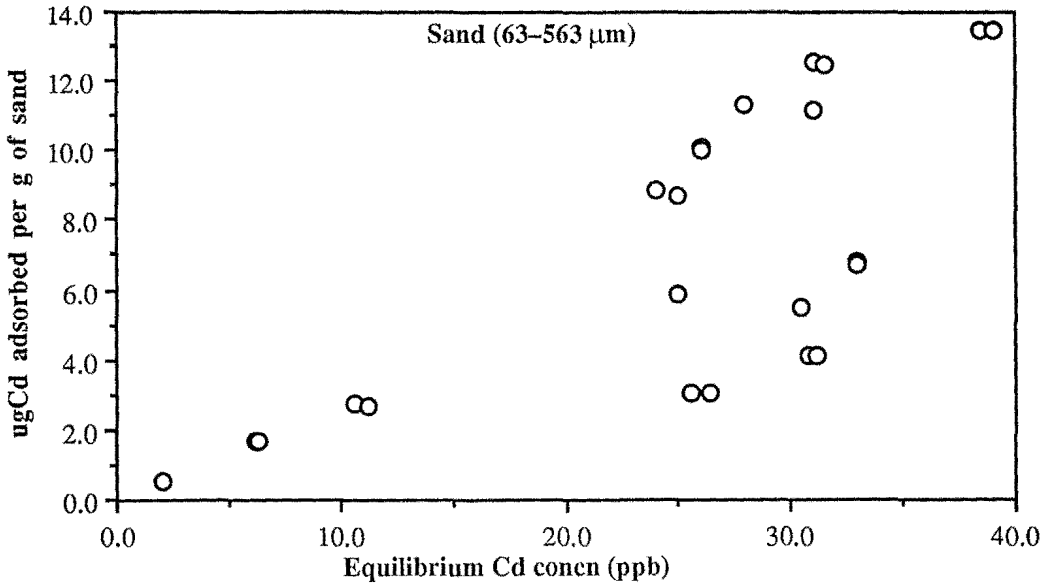
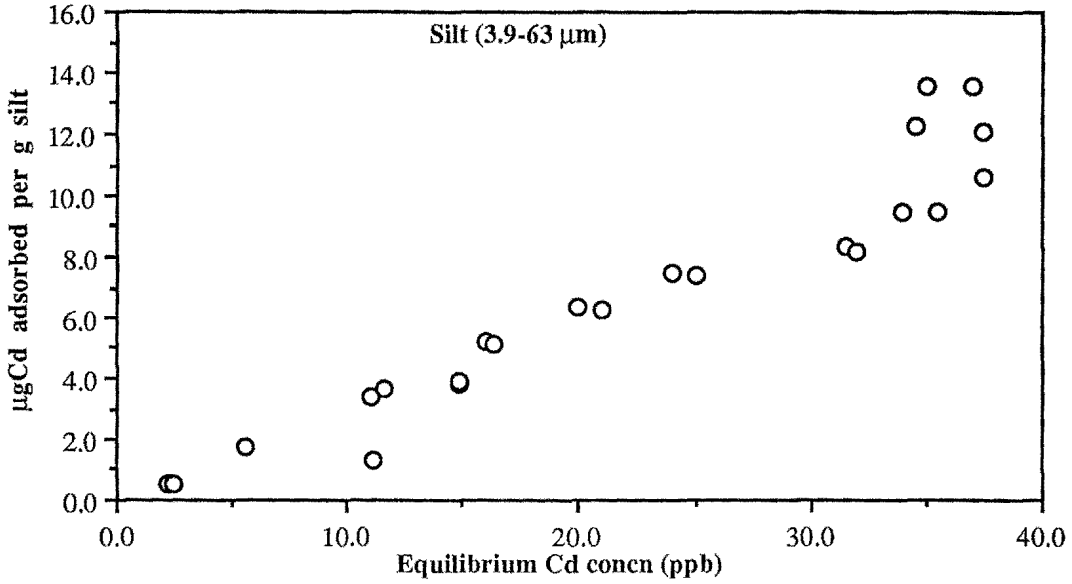


Figure 10·2 continued...



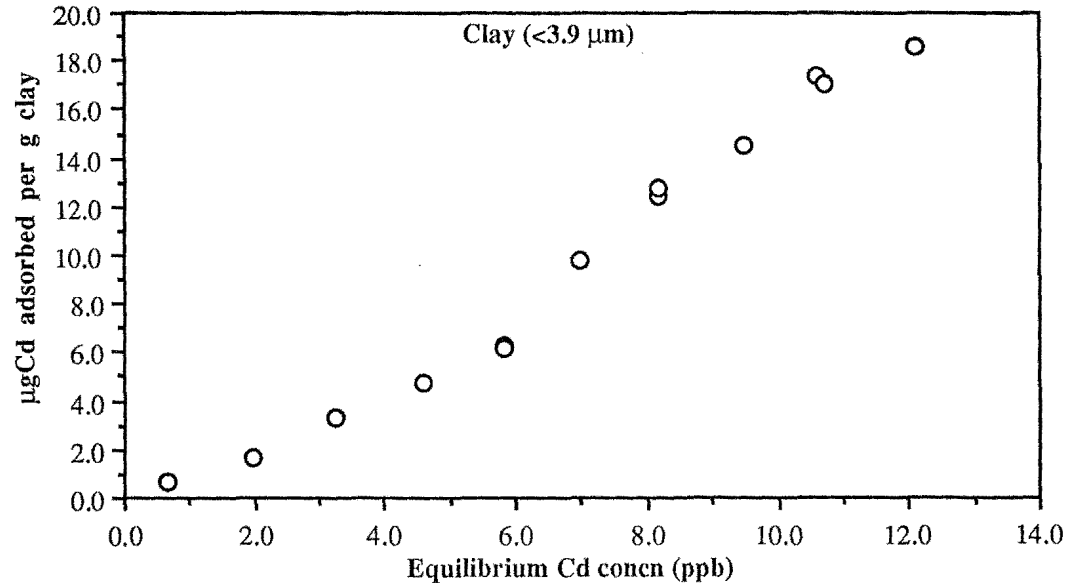
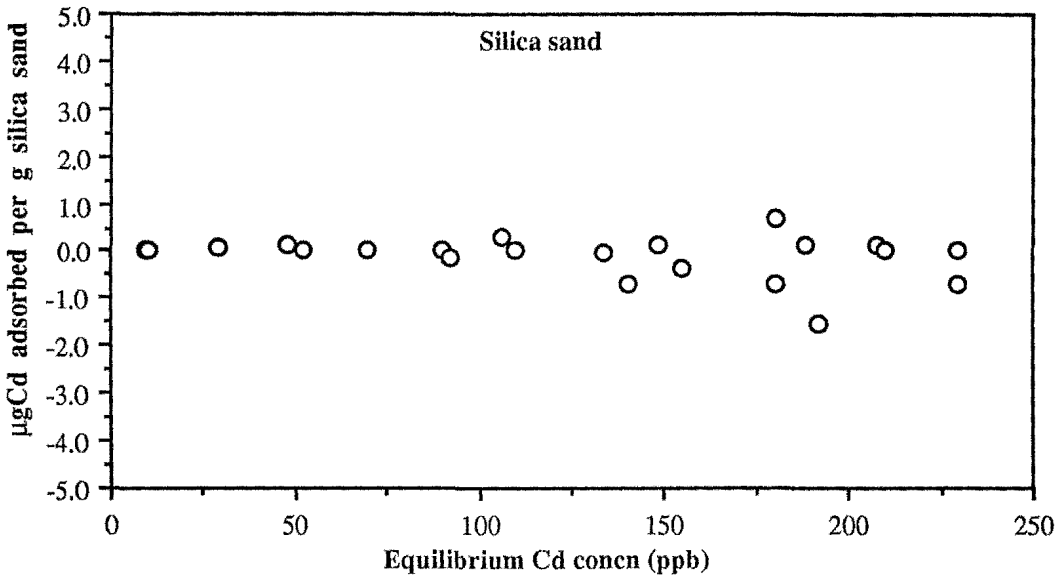


Figure 10·2 continued...



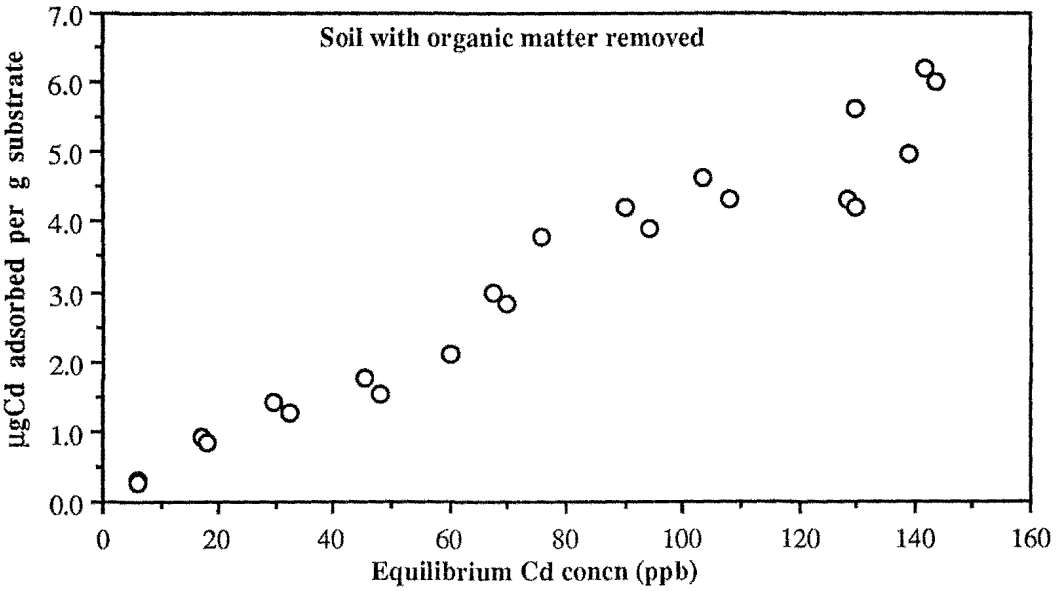


Figure 10·2 continued...

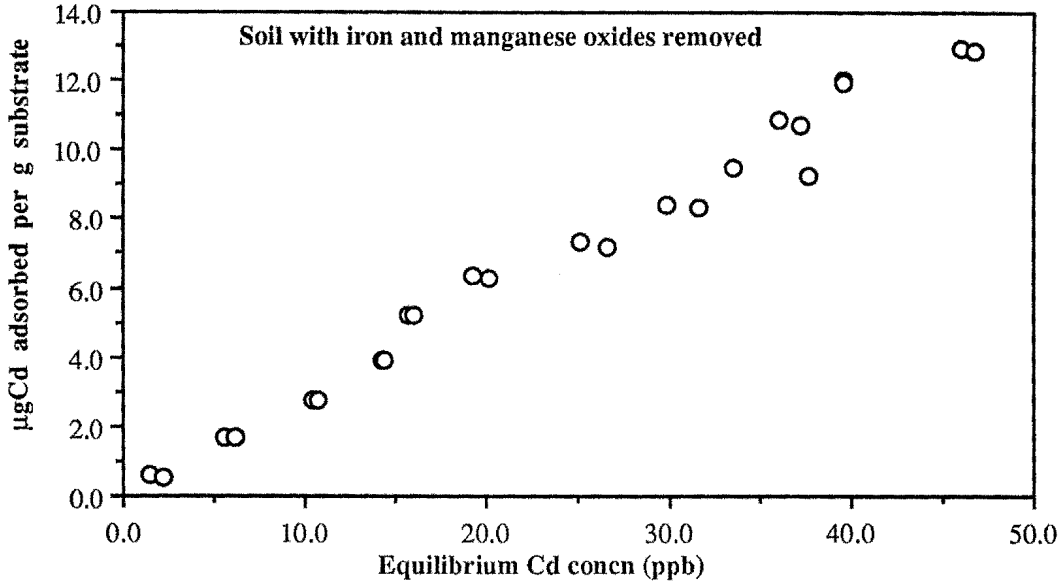


Table 10·3

Means, standard deviations and (Student's t-test) 95% confidence intervals of the conditional equilibrium constants (K*) for cadmium adsorption by, and the percentages of cadmium adsorbed by, Tai Tapu silt loam, its components, and silica sand at pH 5.70 and 25 °C.

Substrate	Percent adsorption (% Adsn)			Cond equilibrium constant (ml g^{-1})		
	Mean	Std dev	95% error	Mean	Std dev	95% error
Whole soil	87.3	4.1	±1.5	528	147	±53
Sand fraction	78.0	7.3	±2.6	277	97	±35
Silt fraction	79.6	4.2	±1.5	284	55	±20
Clay fraction	91.6	2.0	±0.9	840	180	±81
Silica sand	(–0.05)	(4.75)	(±1.70)	(0.6)	(3.8)	(±1.4)
Soil with organic matter removed	37.3	3.5	±1.3	42.1	6.1	±2.2
Soil less iron & manganese oxides	80.4	1.6	±0.6	290	32	±11

The percent of cadmium adsorbed by each fraction follows the order clay (91.6%) > whole soil (87.3%) > soil without iron and manganese oxides (80.4%) > silt (79.6%) > sand (78.0%) > soil without organic material (37.3%) > silica sand (–0.05%) (Table 10·3). A more direct estimate of the contribution which each soil component makes to cadmium adsorption by the whole soil can be made by division of each component's conditional

equilibrium constant by that of the whole soil. These ratios are in the same order, and their values are: clay (1.59) > soil without iron and manganese oxides (0.55) > silt (0.54) > sand (0.52) > soil without organic material (0.08) > silica sand (0.001). However, it should be noted that these differences cannot be interpreted as being entirely due to differences in the intrinsic strength of the (mean) cadmium adsorption bond for each substrate, as they could be caused by different numbers of adsorption sites per unit weight of each substrate (Laxen, 1983).

Of the soil components studied, the clay (<3.5 μm) fraction adsorbed cadmium most strongly. The importance of clay in the determination of soil cadmium adsorption characteristics has been emphasized by a number of workers (Chubin and Street, 1981; Farrah and Pickering, 1977 and 1978; Garcia-Miragaya and Page, 1976 and 1977; Garcia *et al.* 1986; Reid and McDuffie, 1981; Wold and Pickering, 1981). Cadmium can be adsorbed by components of the actual clay minerals (for example, at silicon-oxygen or aluminium-oxygen sites), or by surface coatings of organic material and iron and manganese oxides (Reid and McDuffie, 1981). It has previously been reported that cadmium adsorbed on clay minerals can be mobilized by plants with relative ease (Kabata-Pendias and Pendias, 1985). Adsorption can take the forms both of specific adsorption and complexation.

Silica sand, at the other extreme, adsorbed no cadmium. The inability of silica to adsorb cadmium (and the likely negligible role of silica in cadmium adsorption processes) has also previously been reported by other researchers (Laxen, 1983).

The conditional equilibrium constants describing cadmium adsorption by the silt and sand fractions of the Tai Tapu silt loam are similar, both being about half the value of the conditional equilibrium constant for the whole soil. The clay fraction (<3.5 μm) comprised 22% of the Tai Tapu silt loam, and silt and sand (therefore) comprised 78% of the whole soil. The product obtained by multiplication of the clay fraction's conditional equilibrium constant for cadmium adsorption by 0.22 is (185 ± 19) ml g^{-1}, and that obtained by multiplying the mean of the conditional equilibrium constants for the silt and sand fractions (which are almost identical in value) by 0.78 is (219 ± 44) ml g^{-1}. The sum of these products (*i.e.* the weighted mean) is (404 ± 121) ml g^{-1}, which is (and should be) approximately equal to the conditional equilibrium constant of the whole soil: (528 ± 53) ml g^{-1}. Thus it can be seen that the clay fraction (<3.5 μm), which comprises only 22% of the Tai Tapu silt loam, is likely to be responsible for about 45% of the whole soil's conditional equilibrium constant. The "silt and sand" fraction (3.9–563 μm), which comprises 78% of the soil, is likely to be responsible for about 55% of the overall conditional equilibrium constant.

Removal of iron and manganese oxides from the Tai Tapu silt loam reduced the percent of cadmium adsorbed from 87.3% to 80.4% and the mean conditional equilibrium constant for cadmium adsorption from 528 ml g^{-1} to 290 ml g^{-1}. This suggests that iron and manganese oxides are significant adsorbants of cadmium in Tai Tapu silt loam. Cadmium adsorption characteristics of the dithionite-treated soil were quite similar to those of the soil's silt and sand fractions (Table 10·3 and Figure 10·2). Significant cadmium adsorption by iron

and manganese oxides has previously been reported by Abd-Elfattah and Wada (1981), Chubin and Street (1981) and Garcia-Miragaya and Page (1978).

Removal of organic material from the Tai Tapu silt loam by treatment with hydrogen peroxide had a drastic effect on that substrate's adsorption characteristics, reducing the percent of cadmium adsorbed from 87.3% to 37.3% and the mean conditional equilibrium constant for cadmium adsorption from 528 ml g^{-1} to 42.1 ml g^{-1}. It is worthy of note that part of the reduction in sorptive capacity is likely to have been caused by the partial destruction of some of the soil's clay minerals, manganese oxides and carbonates by the hydrogen peroxide (Van Langeveld *et al.* 1983; Shuman, 1983). Overall, however, it appears probable that the organic component of Tai Tapu silt loam is an extremely important factor governing the amount of cadmium adsorbed by the soil. The organic component (measured by weight loss upon ashing) comprised 12% of the whole soil (Appendix 10·2).

Other researchers' results indicate that the cadmium adsorptive capacity of the organic component of soils or clays differ from region to region, from being largely insignificant (*e.g.* Reid and McDuffie,1981; Petruzzelli *et al.* 1978) to being highly significant (*e.g.* Gerritse and Van Driel, 1984; Haas and Horowitz, 1984; Neal and Sposito, 1986).

Least-squares lines and probabilities of the simple adsorption isotherms were calculated. The adsorption data in Appendices 10·3–10·9 were also plotted according to the (linearized) Langmuir and Freundlich equations (section 10·1·2, equations 7 and 8). The results of these calculations are presented in Table 10·4 (equations of the relationships are given in cases where the probabilities are highly significant).

Table 10·4

Equations and probabilities of simple, Langmuir and Freundlich relationships relating to the adsorption of cadmium on soil and soil components at pH 5.70 and 25 °C.

Substrate	Correlation coefficient	Probability (p)	Significance	Least-squares relationship[a]
Simple equations				
Whole soil	0.955	<0.001	Highly	$\Gamma_{Cd} = 747.29[Cd_{Diss}] - 2.41$
Sand fraction	0.760	<0.001	Highly	$\Gamma_{Cd} = 294.67[Cd_{Diss}] - 0.32$
Silt fraction	0.961	<0.001	Highly	$\Gamma_{Cd} = 321.98[Cd_{Diss}] - 0.48$
Clay fraction	0.987	<0.001	Highly	$\Gamma_{Cd} = 573.77[Cd_{Diss}] + 1.21$
Silica sand	0.298	>0.05	Not	
Soil–organic matter	0.969	<0.001	Highly	$\Gamma_{Cd} = 38.86[Cd_{Diss}] + 0.14$
Soil–Fe & Mn oxides	0.991	<0.001	Highly	$\Gamma_{Cd} = 280.00[Cd_{Diss}] + 0.15$
Langmuir equations				
Whole soil	0.579	<0.01	Very	
Sand fraction	0.073	>0.05	Not	
Silt fraction	0.387	>0.05	Not	
Clay fraction	0.947	<0.001	Highly	$[Cd_{Diss}] / \Gamma_{Cd} = 0.04[Cd_{Diss}]$
Silica sand	0.112	>0.05	Not	

Table 10·4 continued...

Substrate	Correlation coefficient	Probability (p)	Significance	Least-squares relationship[a]
(Langmuir equations contd)				
Soil–organic matter	0.346	>0.05	Not	
Soil–Fe & Mn oxides	0.136	>0.05	Not	
Freundlich equations				
Whole soil	0.949	<0.001	Highly	$\ln\Gamma_{Cd} = 1.19\ln[Cd_{Diss}] + 7.07$
Sand fraction	0.902	<0.001	Highly	$\ln\Gamma_{Cd} = 0.99\ln[Cd_{Diss}] + 5.51$
Silt fraction	0.974	<0.001	Highly	$\ln\Gamma_{Cd} = 1.11\ln[Cd_{Diss}] + 6.08$
Clay fraction	0.991	<0.001	Highly	$\ln\Gamma_{Cd} = 0.83\ln[Cd_{Diss}] + 5.84$
Silica sand	0.834	<0.001	Highly	$\ln\Gamma_{Cd} = 0.88\ln[Cd_{Diss}] - 5.88$
Soil–organic matter	0.988	<0.001	Highly	$\ln\Gamma_{Cd} = 0.93\ln[Cd_{Diss}] + 3.53$
Soil–Fe & Mn oxides	0.994	<0.001	Highly	$\ln\Gamma_{Cd} = 0.97\ln[Cd_{Diss}] + 5.55$

Note: a. Where Γ_{Cd} is in $\mu g\ g^{-1}$ and $[Cd_{Diss}]$ is in $\mu g\ ml^{-1}$.

All the simple adsorption isotherms except for that of silica sand are (statistically) linear (Figure 10·2 and Table 10·4). Because this is the case, the slopes of those of the simple isotherms' least-squares lines which possess near-zero intercepts are approximately equal to the conditional equilibrium constants (K*) (Christensen, 1982; Garcia-Miragaya and Page, 1977). The 95% confidence level intervals of the slopes and intercepts of these simple adsorption isotherms' least-squares lines are given in Appendix 10·10.

A positive intercept on a simple adsorption isotherm indicates that highly specific, high energy adsorption sites are operative at low metal-ion concentrations (Garcia-Miragaya and Page, 1976). Of the soil components investigated at pH 5.70 and 25 °C, only the clay fraction of the Tai Tapu silt loam yielded a simple isotherm with a (statistically) positive least-squares intercept (Appendix 10·10), implying that cadmium-specific sites are likely to comprise a significant portion of the clay fraction. The existence of highly specific cadmium adsorption sites on clays (in addition to cation-exchange-type sites) has been noted by Garcia-Miragaya and Page (1976 and 1977), Garcia *et al.* (1986) and Reid and McDuffie (1981). These authors have suggested that cadmium-specific sites could take the following forms:

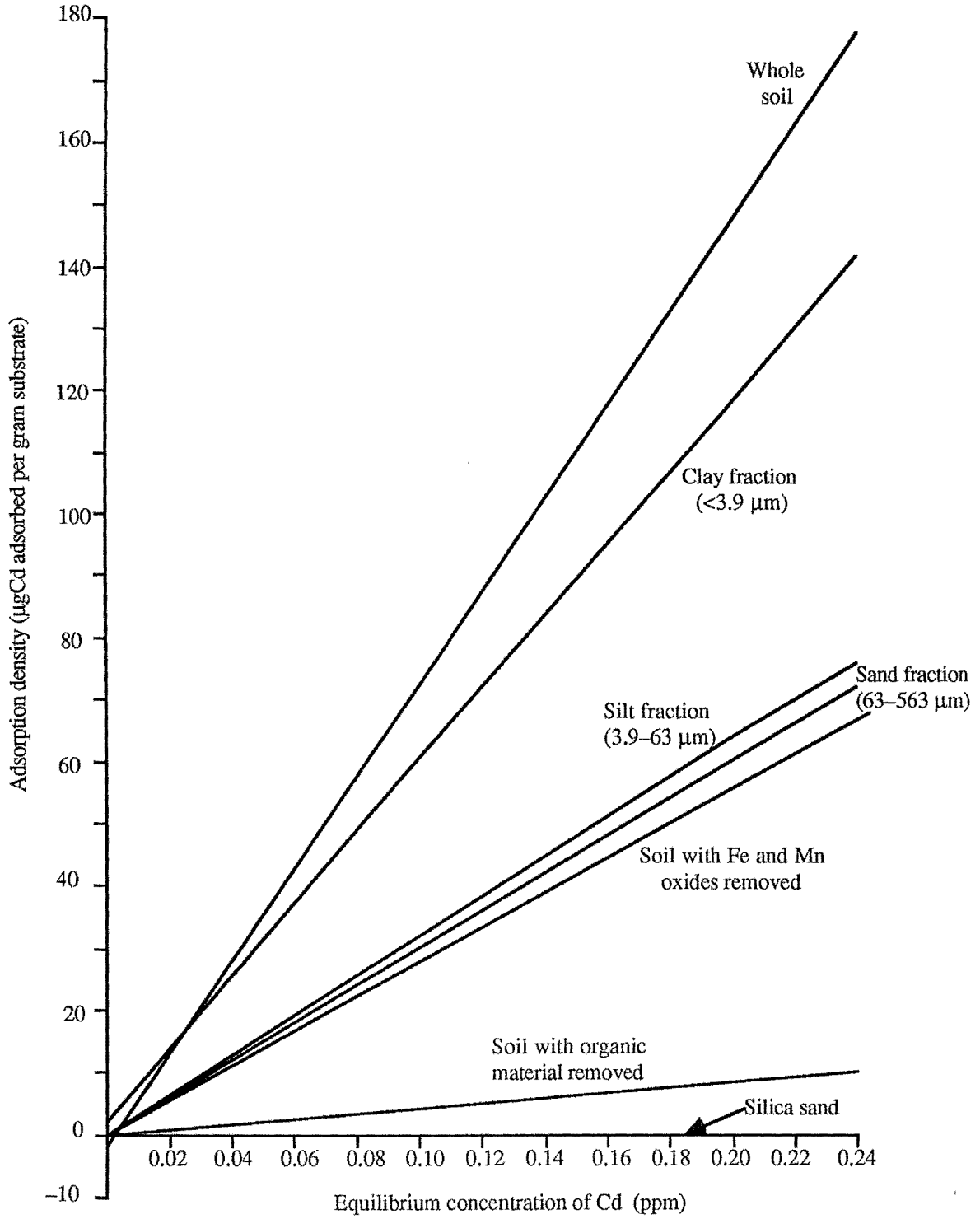
1. Complexation of cadmium by organic matter bound to clay through coordinate-covalent bonding;
2. Chemisorption of cadmium by iron and manganese oxide coatings on clays;
3. Isomorphous replacement of calcium ions comprising part of the clay mineral structure by cadmium ions (Cd^{2+} and Ca^{2+} are of similar size).

Thus, cadmium adsorption onto the clay at pH 5.70 and 25 °C is best described by the combination of a "high-affinity" isotherm with a "constant partition" isotherm; whereas cadmium adsorption by the other soil components and the whole soil are statistically indistinguishable from, and better described by, "constant partition" isotherms.

For purposes of comparison, the least-squares lines of the simple adsorption isotherms are plotted together in Figure 10·3.

Figure 10·3

Comparison of the least-squares equations of the simple adsorption isotherms relating to cadmium adsorption on whole soil and soil components at pH 5.70 and 25 °C.



The Langmuir adsorption model is a suitable description of the adsorption process in the clay fraction of the Tai Tapu silt loam only, whereas the Freundlich adsorption model accurately describes adsorption processes in all seven substrates (Table 10·4). In the case of adsorption by the clay fraction, the linearized Freundlich equation gives the best fit; in the case of the silica sand, the high significance rating of the linearized Freundlich equation fit is thought to be "accidental", both because the intercept is highly negative and because overall, no cadmium was adsorbed by the silica sand (Table 10·3). Thus, it is likely that Tai Tapu silt loam and its components supply a range of dissimilar (*i.e.* non-uniform) cadmium adsorption sites (section 10·1·2).

A Freundlich adsorption isotherm slope of 1.0 would indicate that an increase in the cadmium concentration in solution leads to a directly proportionate increase in the adsorption density (Reid and McDuffie, 1981). The 95% confidence intervals of the slopes and intercepts of the Freundlich plots' least-squares lines (relating to cadmium adsorption by the whole soil and its components) are listed in Table 10·5.

Table 10·5

Slopes and intercepts of the least-squares lines, and their 95% confidence intervals, relating to Freundlich-type adsorption of cadmium on whole soil and its components at pH 5.70 and 25 °C. (The original least-squares equations are given in Table 10·4.)

Substrate	Slope (ln[g ml^{-1}])			Intercept (ln[µg g^{-1}])		
	Mean	Lower limit	Upper limit	Mean	Lower limit	Upper limit
Whole soil	1.19	1.00	1.37	7.07	6.27	7.87
Sand fraction	0.99	0.78	1.20	5.51	4.68	6.34
Silt fraction	1.11	0.99	1.22	6.08	5.46	6.34
Clay fraction	0.83	0.77	0.90	5.84	5.49	6.19
Soil–org matter	0.93	0.87	1.00	3.53	3.35	3.71
Soil–Fe & Mn oxides	0.97	0.92	1.02	5.55	5.35	5.75

It can be seen from the data in Table 10·5 that (at a 95% confidence level) none of the Freundlich plots' least-squares slopes are statistically different from 1.0 except that relating to the clay adsorption isotherm, which has a least-squares slope of 0.83 ± 0.07. This latter result implies that an increase in the cadmium concentration in solution (at pH 5.70 and 25 °C) results in a proportionately smaller increase in the concentration of cadmium in/on the clay. This result is in agreement with those of previous workers (Garcia-Miragaya and Page, 1976 and 1977; Garcia *et al.* 1986; Reid and McDuffie, 1981) Surprisingly, Reid and McDuffie (1981), who studied cadmium adsorption by illite at pH 7.50, also calculated the slope of the Freundlich regression line to be 0.83.

10·3·3 Effect of pH on cadmium adsorption by whole soil

Experiments relating to cadmium adsorption on whole Tai Tapu silt loam at different acidities were carried out at a temperature of 25 °C, an ionic strength of 0.01 and a total solids concentration of 14.3 ± 0.2 g ml^{-1}. The full data sets describing cadmium adsorption by whole Tai Tapu silt loam at pH 7.00 and pH 8.00 are given in Appendices 10·11 and 10·12. Simple adsorption isotherms derived from the data in Appendices 10·11 and 10·12 are presented in Figure 10·4. Statistics summarizing the percentage of cadmium adsorbed by, and the conditional equilibrium constants (K*) for cadmium adsorption by, Tai Tapu silt loam at pH 5.70, pH 7.00 and pH 8.00 are given in Table 10·6.

Figure 10·4

Cadmium adsorption by Tai Tapu silt loam at pH 7.00 and pH 8.00.
(Other parameters are: temperature 25 °C, ionic strength 0.01, total solids concentration (14.3 ± 0.2) g l^{-1}, initial cadmium concentrations in solution 10.0–230 μg l^{-1}.)

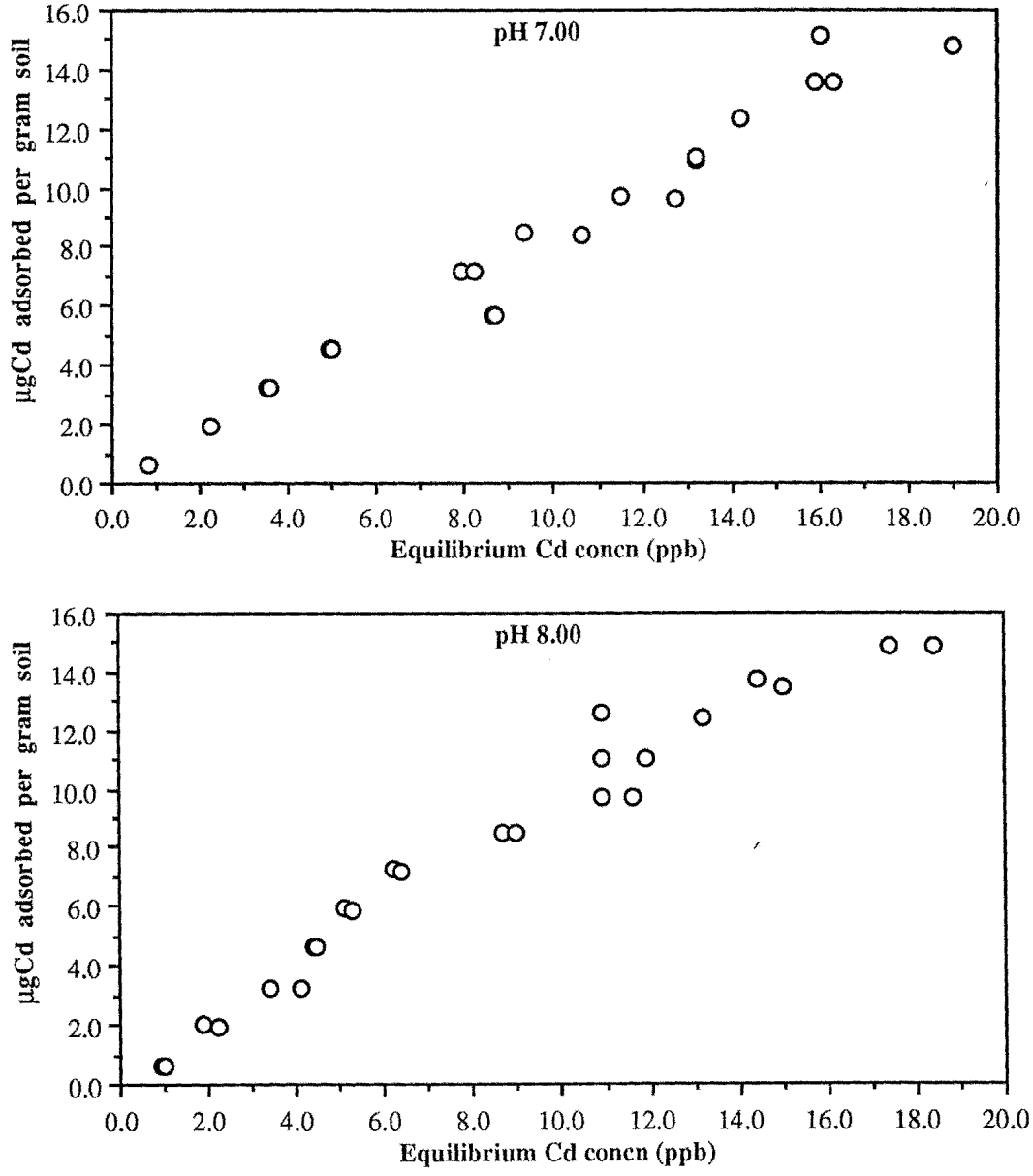


Table 10·6

Means, standard deviations and (Student's t-test) 95% confidence intervals of the percentages of cadmium adsorbed by, and the conditional equilibrium constants (K*) for cadmium adsorption by, whole Tai Tapu silt loam at pH 5.70, pH 7.00 and pH 8.00[a].

pH	Percent adsorption (% Adsn)			Cond equilibrium constant (ml g^{-1})		
	Mean	Std dev	95% error on mean	Mean	Std dev	95% error on mean
5.70	87.3	4.1	±1.5	528	147	±53
7.00	92.2	0.7	±0.3	839	79	±28
8.00	92.9	1.2	±0.4	943	153	±55

Note: **a.** Ionic strength 0.01, total solids concentration (14.3 ± 0.2) g l^{-1}, temperature 25 °C.

Least-squares lines and probabilities of the simple adsorption isotherms at pH 7.00 and pH 8.00, and those of Langmuir and Freundlich plots of the data, were calculated. The results of these calculations are listed in Table 10·7 (equations of the relationships are given in cases where the probabilities are highly significant). Once again, the simple isotherms relating to cadmium adsorption by Tai Tapu silt loam at pH 7.00 and pH 8.00 are (statistically) linear (Table 10·7); their least-squares lines are plotted alongside that describing the cadmium adsorption behaviour of Tai Tapu silt loam at pH 5.70 in Figure 10·5.

Table 10·7

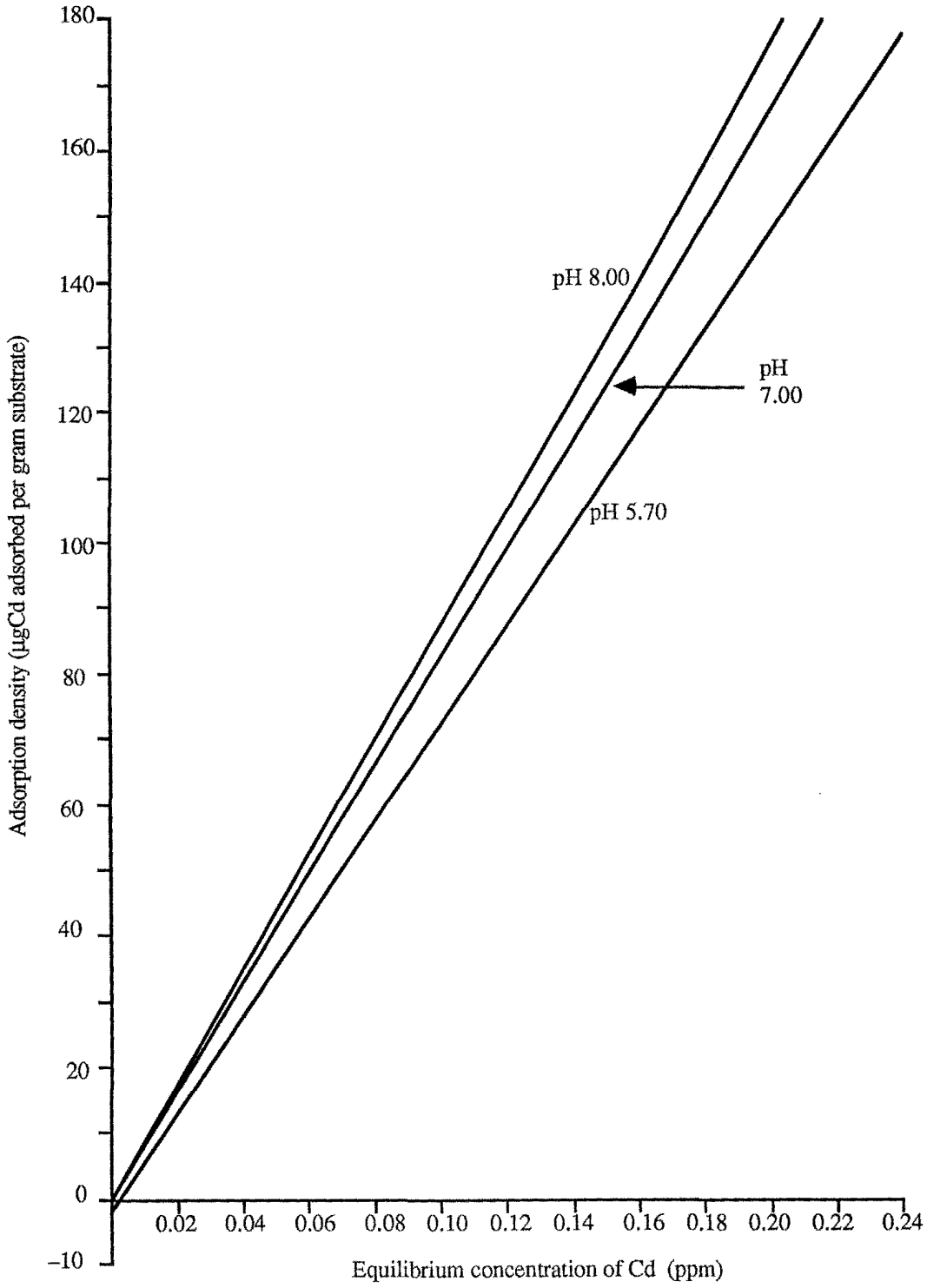
Probabilities of simple, Langmuir and Freundlich relationships relating to the adsorption of cadmium on whole soil at pH 7.00 and pH 8.00; equations are given for highly significant relationships.

	Correlation coefficient	Probability (p)	Significance	Least-squares relationship[a]
Simple equations				
pH 7.00	0.987	<0.001	Highly	$\Gamma_{Cd} = 830.5[Cd_{Diss}] + 0.06$
pH 8.00	0.980	<0.001	Highly	$\Gamma_{Cd} = 863.1[Cd_{Diss}] + 0.70$
Langmuir equations				
pH 7.00	0.359	>0.05	Not	
pH 8.00	0.090	>0.05	Not	
Freundlich equations				
pH 7.00	0.994	<0.001	Highly	$\ln\Gamma_{Cd} = 1.00\ln[Cd_{Diss}] + 7.63$
pH 8.00	0.986	<0.001	Highly	$\ln\Gamma_{Cd} = 1.06\ln[Cd_{Diss}] + 7.16$

Note: **a.** Where Γ_{Cd} is in μg g^{-1} and $[Cd_{Diss}]$ is in μg ml^{-1}.

Figure 10·5

Comparison of the least-squares equations of the simple adsorption isotherms for cadmium adsorption on whole Tai Tapu silt loam at pH 5.70, pH 7.00 and pH 8.00. (Other parameters are: temperature 25 °C, ionic strength 0.01, total solids concentration 14.2 ± 0.2 g l^{-1}.)



It can be seen from the data in Table 10·6 that raising the pH from 5.70 to 8.00 causes the percent of cadmium adsorbed from solution by Tai Tapu silt loam to increase from 87.3% to 92.9%, and the conditional equilibrium constant for the adsorption process to increase from 528 g ml^{-1} to 943 g ml^{-1}. The extent of cadmium adsorption appears to increase abruptly upon raising the pH from 5.70 to 7.00, but then level-off upon further increasing the pH to 8.00 (Table 10·6 and Figure 10·5). These trends are in general agreement with those reported by other workers (Abd-Elfattah and Wada, 1981; Christensen, 1984; Elliot, 1983; Farrah and Pickering, 1977; Gerritse and Van Driel, 1984; Garcia-Miragaya and Page, 1977). The general decrease in the amount of cadmium adsorbed with increasing acidity is thought to be due to the higher acidities causing both increased competition for sites by hydrogen ions and an increase in the aggregate positive charge of the clay edge sites.

It is unlikely that hydrolysis of cadmium contributed significantly to its removal from solution, as cadmium hydrolysis begins *above* pH 8 (Hahne and Kroontje, 1973).

Once again, adsorption isotherms for cadmium on whole soil at pH 7.00 and pH 8.00 show good fits both to simple linear regression lines and linearized Freundlich plots, but are not well described by the Langmuir adsorption model (Table 10·7). The 95% confidence intervals on the slopes and intercepts of the significant regression lines are listed in Appendix 10·13.

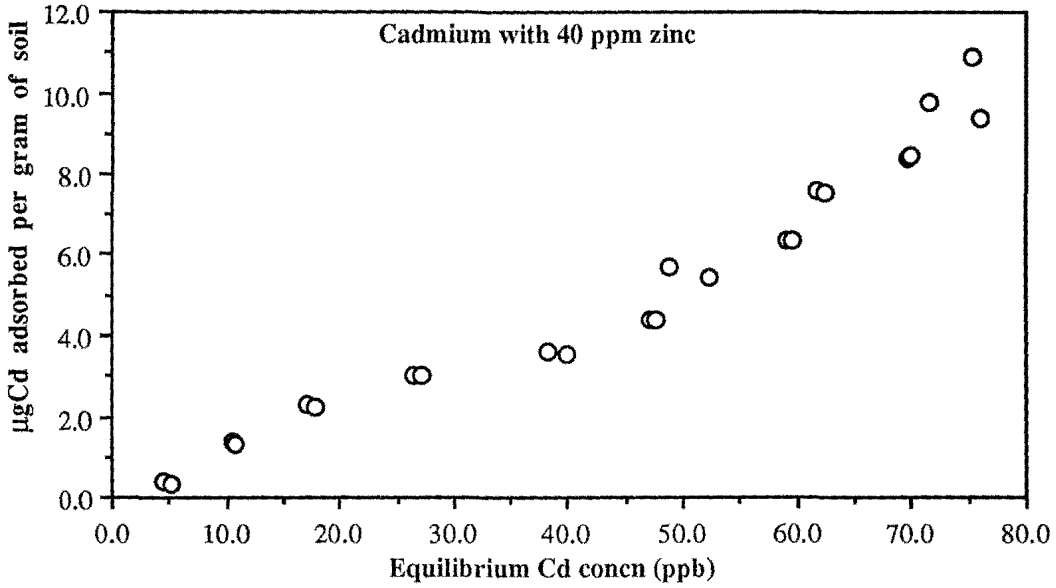
Slopes of the Freundlich least-squares lines for cadmium adsorption on Tai Tapu silt loam at pH 7.00 and pH 8.00 are statistically indistinguishable from 1.0 (as was that relating to cadmium adsorption on whole soil at pH 5.70) again implying that an increase in cadmium concentrations in solution will cause an increase of similar magnitude in cadmium levels in the soil (Table 10·7 and Appendix 10·13). Soil at pH 8.00 apparently had a higher affinity for trace concentrations of cadmium than soil at pH 5.70 or 7.00, as the least-squares line's intercept of its simple isotherm is statistically positive (Table 10·7 and Appendix 10·13). Additionally, the mean values of the intercepts of the simple isotherms' regression lines increase with increasing pH, and are –2.41 μg g^{-1} at pH 5.70, 0.06 μg g^{-1} at pH 7.00, and 0.70 μg g^{-1} at pH 8.00 (Tables 10·5 and 10·7). It is probable that, within the pH range 5.70 to 8.00, an increase in the pH causes a greater proportion of the high energy cadmium-specific sites in the Tai Tapu silt loam to become activated.

10·3·4 Competitive adsorption

The data sets describing cadmium adsorption by Tai Tapu silt loam in the presence of 40 μgZn ml^{-1} and in the presence of 3 μgPb ml^{-1} are given in Appendices 10·14 and 10·15. These experiments were carried out at a pH of 5.70, a temperature of 25 °C, an ionic strength of 0.01 and a total solids concentration of 14.3 ± 0.2 g ml^{-1}. Simple cadmium adsorption isotherms derived from the data in Appendices 10·14 and 10·15 are presented in Figure 10·6. Statistics summarizing the percentage of cadmium adsorbed, and the conditional equilibrium constants (K*) for cadmium adsorption under these conditions are given in Table 10·8.

Figure 10·6

Cadmium adsorption by Tai Tapu silt loam in the presence of zinc and of lead.
(Other parameters are: pH 5.70, temperature 25 °C, ionic strength 0.01, total solids concentration (14.3 ± 0.2) g l^{-1}, initial cadmium concentrations in solution 10.0–230 μg l^{-1}.)



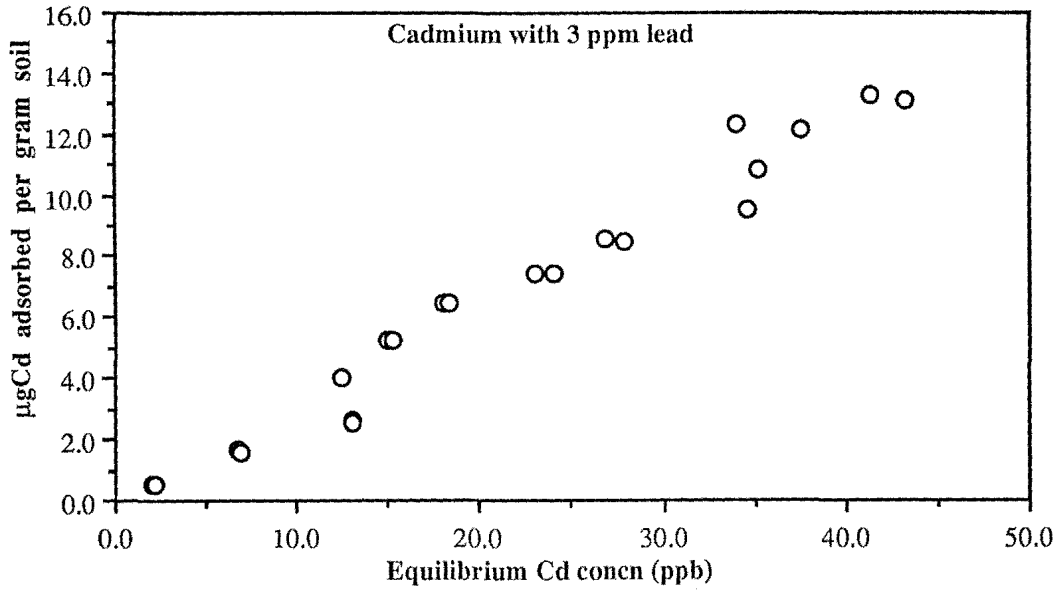


Table 10·8

Means, standard deviations and (Student's t-test) 95% confidence intervals of the percentages adsorbed and the conditional equilibrium constants for the competitive adsorption of cadmium with zinc, and cadmium with lead, on Tai Tapu silt loam[a].

	Percent adsorption (% Adsn)			Cond equilibrium constant (ml g^{-1})		
	Mean	Std dev	95% error on mean	Mean	Std dev	95% error on mean
Cadmium and zinc[b]						
Cadmium	61.5	4.3	±1.6	114	19	±7
Zinc	42.4	2.4	±0.9	52	6	±2
Cadmium and lead[c]						
Cadmium	80.7	2.8	±1.0	300	47	±17
Lead	93.8	0.5	±0.2	992	282	±100

Notes: **a.** pH 5.70, ionic strength 0.01, total solids concentration (14.3 ± 0.2) g l^{-1}, temperature 25 °C.
b. 40μgZn ml^{-1}.
c. 3 μgPb ml^{-1}.

Least-squares lines and probabilities of the simple adsorption isotherms, and those of the Langmuir and Freundlich plots, for cadmium adsorption by Tai Tapu silt loam in the presence of lead and zinc were calculated; probabilities (and equations of the highly significant relationships) are listed in Table 10·9. The least-squares lines of the simple isotherms (which are linear) are plotted alongside that describing the cadmium adsorption behaviour of Tai Tapu silt loam in the absence of competing cations in Figure 10·7.

Table 10·9

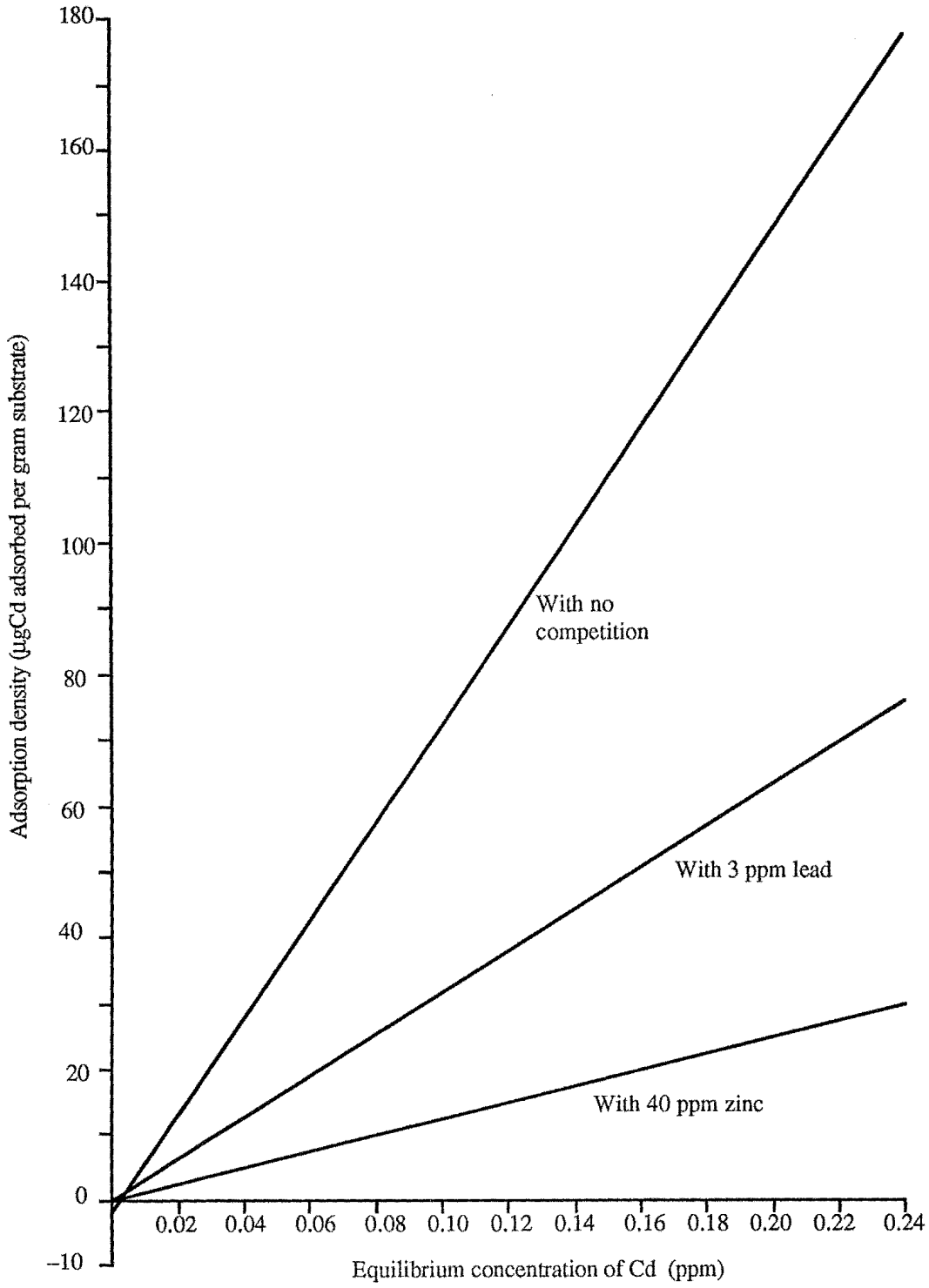
Probabilities of simple, Langmuir and Freundlich relationships relating to the adsorption of cadmium on Tai Tapu silt loam in the presence of zinc (40 μgZn ml^{-1}) and in the presence of lead (3 μgPb ml^{-1}); equations are given for highly significant relationships.

	Correlation coefficient	Probability (p)	Significance	Least-squares relationship[a]
Simple equations				
Cd and Zn	0.970	<0.001	Highly	$\Gamma_{Cd} = 130.5[Cd_{Diss}] - 0.57$
Cd and Pb	0.982	<0.001	Highly	$\Gamma_{Cd} = 317.6[Cd_{Diss}] - 0.19$
Langmuir equations				
Cd and Zn	0.428	<0.05	Just	
Cd and Pb	0.396	>0.05	Not	
Freundlich equations				
Cd and Zn	0.985	<0.001	Highly	$\ln\Gamma_{Cd} = 1.09\ln[Cd_{Diss}] + 5.03$
Cd and Pb	0.986	<0.001	Highly	$\ln\Gamma_{Cd} = 1.09\ln[Cd_{Diss}] + 6.04$

Note: **a.** Where Γ_{Cd} is in μg g^{-1} and $[Cd_{Diss}]$ is in μg ml^{-1}.

Figure 10·7

Comparison of the least-squares equations of the simple adsorption isotherms describing cadmium adsorption on whole soil in the presence of zinc and lead (at pH 5.70 and 25 °C).



Initial lead and zinc concentrations of 3 $\mu g\ ml^{-1}$ and 40 $\mu g\ ml^{-1}$ (respectively) were chosen because (at a mean initial cadmium concentration of 0.12 $\mu g\ ml^{-1}$) the mean ratios of the zinc concentration to the cadmium concentration, and the lead concentration to the cadmium concentration, were more or less the same as those which were present in the Avon and Heathcote River water samples (Table 9·4 in section 9·3·1).

Tai Tapu silt loam exhibits a very strong affinity for lead at natural soil pH values: a mean value of 93.8% of the (3 $\mu g\ ml^{-1}$) added lead was adsorbed by the soil (Table 10·8). This had the effect of reducing the percent of cadmium adsorbed from 87.3% to 80.7%.

Comparison of the conditional equilibrium constants should in this case be undertaken with more care, as they tend to decrease in value with increasing metal ion concentration (the concentration of lead in solution was 13–300 times higher than that of cadmium) (Table 10·1). Interestingly however, the conditional equilibrium constant for lead adsorption by Tai Tapu silt loam is 3.3 times higher than that for cadmium adsorption despite the fact that lead concentrations in solution were also significantly higher than those of cadmium (Table 10·8). This implies that the soil's intrinsic affinity for lead is likely to be substantially greater than its intrinsic affinity for cadmium.

The addition of 40 $\mu gZn\ ml^{-1}$ to the solution caused the amount of cadmium adsorbed to fall from 87.3% to 61.5% (Table 10·8); a mean value of 42.4% of the added zinc was adsorbed by the soil. Concentrations of zinc in solution were 173–4 000 times higher than those of cadmium; under these conditions, the conditional equilibrium constant for zinc adsorption by Tai Tapu silt loam is 2.2 times less than that for cadmium adsorption.

Thus, initial concentrations of lead and zinc in solution which were higher than cadmium concentrations by similar amounts to zinc/cadmium and lead/cadmium ratios in Avon and Heathcote River water samples caused significant reductions in the amount of cadmium adsorbed by Tai Tapu silt loam, suggesting that in natural systems, cadmium mobility in soils is likely to be enhanced by the presence of other metallic species.

As was the case in sections 10·3·2 and 10·3·2, simple and Freundlich-type adsorption isotherms for cadmium on whole soil in the presence of zinc and lead are linear, whereas the data is not well described by the Langmuir adsorption model (Table 10·9). The 95% confidence intervals on the slopes and intercepts of the significant regression lines are listed in Appendix 10·16.

Intercepts of the simple isotherms' least-squares lines for cadmium adsorption on Tai Tapu silt loam in the presence of zinc and lead are statistically indistinguishable from zero. Similarly, slopes of the Freundlich plots' least-squares lines are statistically indistinguishable from 1.0 (Table 10·9 and Appendix 10·13).

10·4 Conclusion

Tai Tapu silt loam has a strong affinity for trace amounts of cadmium, and adsorbed about nine-tenths (87.3%) of the available cadmium (0.010–0.230 μgCd ml^{-1}) at its natural pH of 5.70. This suggests that the mobility of cadmium in Tai Tapu silt loam would be limited. The conditional equilibrium constant for cadmium adsorption by the whole soil at pH 5.70, ionic strength of 0.01, temperature of 25 °C and a total solids concentration of (14.3 ± 0.2) g ml^{-1} was found to be (528 ± 53) ml g^{-1}.

The amounts of cadmium adsorbed by the various fractions of Tai Tapu silt loam under identical conditions follow the order clay (91.6%) > soil without iron and manganese oxides (80.4%) > silt (79.6%) > sand (78.0%) > soil without organic material (37.3%) > silica sand (–0.05%). The ratios obtained by dividing the conditional equilibrium constants by that for cadmium adsorption on the whole Tai Tapu silt loam follow the same order, and are: clay (1.59) > soil without iron and manganese oxides (0.55) > silt (0.54) > sand (0.52) > soil without organic material (0.08) > silica sand (0.001).

It is estimated that the clay fraction (<3.5 μm), which comprises only 22% of the Tai Tapu silt loam, is likely to be responsible for about 45% of the whole soil's conditional equilibrium constant, whereas the "silt and sand" fraction (3.9–563 μm), which comprises 78% of the soil, is likely to be responsible for about 55% of the overall conditional equilibrium constant. It has been reported previously that cadmium adsorbed on clays can be mobilized by plants with relative ease.

Raising the pH from 5.70 to 8.00 caused the amount of cadmium adsorbed from solution by whole Tai Tapu silt loam to increase from 87.3% to 92.9%, and the conditional equilibrium constant for the adsorption process to increase from 528 g ml^{-1} to 943 g ml^{-1}.

Addition of 3 μgPb ml^{-1} to the equilibration solutions had the effect of reducing cadmium adsorption from 87.3% to 80.7%. Addition of 40 μgZn ml^{-1} to the solution caused cadmium adsorption to fall from 87.3% to 61.5%. These initial concentrations of lead and zinc in solution were higher than solution cadmium concentrations by similar amounts to zinc/cadmium and lead/cadmium ratios in Avon and Heathcote River water samples. The significant reductions in the amount of cadmium adsorbed by Tai Tapu silt loam under these conditions suggests that in natural systems, cadmium mobility in soils is likely to be enhanced by the presence of other metallic species.

All the simple adsorption isotherms except for that of silica sand are linear. Cadmium adsorption by the clay at pH 5.70 and 25 °C, and by the whole soil at pH 8.00 and 25 °C, is best described (in each case) by the combination of a "high-affinity" isotherm with a "constant partition" isotherm; whereas cadmium adsorption under all the other conditions examined is better described by simple "constant partition" isotherms.

The Langmuir adsorption model is a suitable description of the adsorption process in the clay fraction of the Tai Tapu silt loam only, whereas the Freundlich adsorption model accurately describes adsorption processes in all the substrates examined (and under all the

experimental conditions used). Thus, it is likely that Tai Tapu silt loam and its components supply a range of dissimilar (*i.e.* non-uniform) cadmium adsorption sites.

None of the Freundlich least-squares slopes are statistically different from 1.0 except that relating to the clay adsorption isotherm, which has a least-squares slope of 0.83 ± 0.07. These results show that in the case of the clay (at pH 5.70 and 25 °C), an increase in the cadmium concentration in solution results in a proportionately smaller increase in the concentration of cadmium in/on the clay, and that for each of the other substrates examined, a higher cadmium concentration in solution results in a similar magnitude increase in the cadmium concentration of the solid phase.

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10·6 Appendices

Appendix 10·1 (section 10·2·1)

Comparison of the d-spacings (Å) and relative intensities[a] of the X-ray diffraction peaks from samples of clay, silt and sand isolated from Tai Tapu silt loam with those given in the literature[b] for quartz, trioctahedral illite, and low-albite.

D-spacings (Å)					
Clay (<3.9 μm)	Silt (3.9–63 μm)	Sand (63–563 μm)	Illite	Quartz	Low-albite
10.0_2			10.0_{10}		
7.06_1					
4.47_2			4.48_9		
4.25_2	4.25_2	4.26_2		4.26_4	
4.02_1	4.03_1	4.03_1			4.02_6
3.76_1	3.76_1	3.77_1			3.78_3
3.66_1	3.66_1	3.67_1			3.66_3
3.34_{10}	3.34_{10}	3.34_{10}	3.33_9	3.34_{10}	
3.18_2	3.18_2	3.20_2			3.19_{10}, 3.21_6
	2.97_1				
	2.96_1				
2.59_1	2.59_1	2.57_1	2.61_6		
2.45_1	2.45_1	2.46_1		2.46_1	
			(2.42_4)		
2.28_1				2.28_1	
2.12_1	2.12_1			2.13_1	
2.08_1					
1.98_1		1.98_1			
1.82_1				1.82_2	

Notes: **a.** Intensities in the samples of clay, silt and sand are relative to the extremely intense peak of quartz at 3.34 Å.
b. Source of d-spacings for illite, quartz and low-albite: Brindley and Brown, 1980.

Appendix 10·2 (section 10·2·1)

Organic content and concentrations of cadmium, lead and zinc in Tai Tapu silt loam and in its silt and clay size fractions.

Parameter	Whole soil	Clay <3.9 μm	Silt 3.9–63 μm
Organic content (%)	12.1	13.3	8.17
Cd concn ($\mu g\ g^{-1}$)	0.096	0.123	0.090
Pb concn ($\mu g\ g^{-1}$)	92.8	145	95.4
Zn concn ($\mu g\ g^{-1}$)	70.1	120	60.3

Appendix 10·3 (section 10·3·2)

Parameters relating to the adsorption of 10.0–230 μgCd l^{-1} solution on whole Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6[a]
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[Solid$_T$] (mg l^{-1})	14 208	14 437	14 426	14 180	14 314	14 400
Equilibrium Cd concn (μg l^{-1})	1.3	1.3	6.0	6.5	11.2	19.3
Error[b] (μg l^{-1})	±0.08	±0.04	±0.20	±0.24	±0.33	±0.58
% Adsn	87.0	86.8	80.2	78.3	77.6	61.4
Adsn density (Γ_{Cd}) (μg g^{-1})	0.612	0.601	1.67	1.66	2.71	2.13
[SCd] / [Cd$_{Diss}$]	6.69	6.58	4.05	3.61	3.46	1.59
K* (ml g^{-1})	471	455	281	254	242	110

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[Solid$_T$] (mg l^{-1})	14 343	14 266	14 206	14 286	14 306	14 314
Equilibrium Cd concn (μg l^{-1})	11.2	12.0	12.4	12.5	12.4	12.0
Error[b] (μg l^{-1})	±0.2	±0.1	±0.5	±0.3	±1.0	±0.9
% Adsn	84.0	82.8	86.2	86.1	89.1	89.1
Adsn density (Γ_{Cd}) (μg g^{-1})	4.10	4.07	5.46	5.43	6.82	6.84
[SCd] / [Cd$_{Diss}$]	5.25	4.81	6.25	6.19	8.17	8.17
K* (ml g^{-1})	366	337	440	434	571	571

Appendix 10·3 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 134	14 251	14 220	14 131	14 234	14 266
Equilibrium Cd concn ($\mu g\ l^{-1}$)	14.0	12.8	15.2	14.8	16.6	17.0
Error[b] ($\mu g\ l^{-1}$)	±0.3	±0.4	±0.9	±0.3	±0.2	±0.2
% Adsn	89.2	90.2	89.9	90.1	90.2	90.0
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	8.21	8.22	9.48	9.57	10.8	10.7
[SCd] / [Cd$_{Diss}$]	8.26	9.20	8.90	9.10	9.20	9.00
K* ($ml\ g^{-1}$)	584	646	626	644	647	631

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 274	14 280	14 200	14 246	14 183	14 346
Equilibrium Cd concn ($\mu g\ l^{-1}$)	18.4	17.8	20.0	20.0	23.0	22.5
Error[b] ($\mu g\ l^{-1}$)	±2.0	±0.5	±0.9	±2.0	±1.2	±0.9
% Adsn	90.3	90.6	90.5	90.5	90.0	90.2
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	12.0	12.1	13.4	13.3	14.6	14.5
[SCd] / [Cd$_{Diss}$]	9.31	9.63	9.53	9.53	9.00	9.20
K* ($ml\ g^{-1}$)	652	675	671	669	635	642

Notes: **a.** Assumed to be an outlier.
b. Student's t-test 95% error on analytically determined concentration.

Appendix 10·4 (section 10·3·2)

Parameters relating to the adsorption of 10.0–230 μgCd l^{-1} solution on the sand (63–563 μm) fraction of Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 429	14 454	14 311	14 291	14 257	14 349
Equilibrium Cd concn (μg l^{-1})	2.1	2.1	6.3	6.2	10.6	11.2
Error[a] (μg l^{-1})	±0.3	±0.2	±0.2	±0.3	±0.2	±0.2
% Adsn	79.5	79.5	79.0	79.3	78.8	77.6
Adsn density (Γ_{Cd}) (μg g^{-1})	0.551	0.550	1.66	1.67	2.76	2.70
[SCd] / [Cd_{Diss}]	3.88	3.88	3.76	3.83	3.72	3.46
K* (ml g^{-1})	269	268	263	268	261	241

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] (mg l^{-1})	14 429	14 440	14 243	14 234	14 354	14 406
Equilibrium Cd concn (μg l^{-1})	26.4	25.6	30.8	31.2	25.0	30.5
Error[a] (μg l^{-1})	±1.7	±1.6	±2.9	±0.9	±0.3	±2.2
% Adsn	62.3	63.4	65.8	65.3	77.3	72.3
Adsn density (Γ_{Cd}) (μg g^{-1})	3.02	3.08	4.16	4.13	5.92	5.52
[SCd] / [Cd_{Diss}]	1.65	1.73	1.92	1.88	3.41	2.61
K* (ml g^{-1})	115	120	135	132	237	181

Appendix 10·4 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[$Solid_T$] ($mg\ l^{-1}$)	14 300	14 366	14 271	14 254	14 249	14 386
Equilibrium Cd concn ($\mu g\ l^{-1}$)	33.0	33.1	25.0	24.0	26.0	26.0
Error[a] ($\mu g\ l^{-1}$)	±0.8	±1.8	±0.9	±0.6	±0.2	±1.6
% Adsn	74.6	74.6	83.3	84.0	84.7	84.7
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	6.78	6.75	8.76	8.84	10.1	10.0
[SCd] / [Cd_{Diss}]	2.94	2.94	4.99	5.25	5.54	5.54
K* ($ml\ g^{-1}$)	205	204	350	368	389	385

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[$Solid_T$] ($mg\ l^{-1}$)	14 237	14 294	14 266	14 303	14 214	14 217
Equilibrium Cd concn ($\mu g\ l^{-1}$)	31.0	28.0	31.0	31.5	38.5	39.0
Error[a] ($\mu g\ l^{-1}$)	±0.7	±0.2	±2.1	±1.4	±1.9	±1.7
% Adsn	83.7	85.3	85.0	85.0	83.3	83.3
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	11.2	11.3	12.5	12.5	13.5	13.4
[SCd] / [Cd_{Diss}]	5.14	5.80	5.67	5.67	4.99	4.88
K* ($ml\ g^{-1}$)	361	406	397	396	351	343

Note: a. Student's t-test 95% error on analytically determined concentration.

Appendix 10·5 (section 10·3·2)

Parameters relating to the adsorption of 10.0–230 μgCd l^{-1} solution on the silt (3.9–63 μm) fraction of Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn ($\mu g\ l^{-1}$)	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] ($mg\ l^{-1}$)	14 454	14 326	14 200	14 351	14 457	14 263
Equilibrium Cd concn ($\mu g\ l^{-1}$)	2.4	2.3	5.6	11.1	11.6	11.0
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.2	±0.2	±0.2	±1.0	±1.1
% Adsn	76.0	77.5	81.3	63.0	76.8	78.0
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	0.526	0.541	1.72	1.32	3.69	3.43
[SCd] / [Cd_{Diss}]	3.17	3.44	4.35	1.70	3.31	3.54
K* ($ml\ g^{-1}$)	219	240	306	119	229	249

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn ($\mu g\ l^{-1}$)	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] ($mg\ l^{-1}$)	14 366	14 257	14 229	14 311	14 254	14 297
Equilibrium Cd concn ($\mu g\ l^{-1}$)	14.8	14.8	16.0	16.4	20.0	21.0
Error[a] ($\mu g\ l^{-1}$)	±0.3	±2.7	±0.6	±0.7	±0.9	±0.2
% Adsn	78.9	78.9	82.2	81.8	81.8	80.9
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	3.84	3.87	5.20	5.14	6.31	6.23
[SCd] / [Cd_{Diss}]	3.74	3.74	4.62	4.50	4.50	4.24
K* ($ml\ g^{-1}$)	260	262	325	314	315	296

Appendix 10·5 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[$Solid_T$] ($mg\ l^{-1}$)	14 206	14 220	14 143	14 394	14 286	14 166
Equilibrium Cd concn ($\mu g\ l^{-1}$)	25.0	24.0	31.5	32.0	34.0	35.5
Error[a] ($\mu g\ l^{-1}$)	±0.2	±2.3	±1.1	±2.6	±1.3	±1.0
% Adsn	80.8	81.5	79.0	78.6	80.0	79.1
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	7.39	7.45	8.38	8.20	9.52	9.50
[SCd] / [Cd_{Diss}]	4.21	4.41	3.76	3.67	4.00	3.79
K* ($ml\ g^{-1}$)	296	310	266	255	280	267

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[$Solid_T$] ($mg\ l^{-1}$)	14 351	14 349	14 283	14 291	14 417	14 254
Equilibrium Cd concn ($\mu g\ l^{-1}$)	37.5	37.5	37.5	34.5	35.0	37.0
Error[a] ($\mu g\ l^{-1}$)	±1.0	±0.4	±1.7	±0.4	±1.1	±1.4
% Adsn	80.3	80.3	82.1	83.6	84.8	83.9
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	10.6	10.6	12.1	12.3	13.5	13.5
[SCd] / [Cd_{Diss}]	4.08	4.08	4.59	5.10	5.58	5.21
K* ($ml\ g^{-1}$)	284	284	321	357	387	366

Note: **a**. Student's t-test 95% error on analytically determined concentration.

Appendix 10·6 (section 10·3·2)

Parameters relating to the adsorption of 10.0–190 μgCd l^{-1} solution on the clay (<3.9 μm) fraction of Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number							
	1	2	3	4	5	6	7	8
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	50.0	50.0	70.0	90.0	90.0
[$Solid_T$] (mg l^{-1})	14 314	14 203	14 217	14 429	14 429	14 191	14 360	14 371
Equilibrium Cd concn (μg l^{-1})	0.7	0.7	1.7	3.3	3.3	4.8	6.2	6.3
Error[a] (μg l^{-1})	±0.2	±0.2	±0.2	±0.2	±0.2	±0.2	±0.3	±0.6
% Adsn	93.3	93.3	94.3	93.4	93.4	93.2	93.1	93.1
Adsn density (Γ_{Cd}) (μg g^{-1})	0.651	0.657	1.99	3.24	3.24	4.60	5.84	5.83
[SCd] / [Cd_{Diss}]	13.9	13.9	16.5	14.2	14.2	13.7	13.5	13.5
K* (ml g^{-1})	973	981	1 160	981	981	966	940	939

Parameter	Sample number						
	9	10	11	12	13	14	15
Initial Cd concn (μg l^{-1})	110	130	130	150	170	170	190
[$Solid_T$] (mg l^{-1})	14 337	14 383	14 303	14 271	14 309	14 394	14 209
Equilibrium Cd concn (μg l^{-1})	9.8	12.4	12.8	14.5	17.0	17.4	18.6
Error[a] (μg l^{-1})	±0.3	±0.4	±0.3	±0.8	±0.4	±0.1	±0.6
% Adsn	91.1	90.5	90.2	90.3	90.0	89.8	90.2
Adsn density (Γ_{Cd}) (μg g^{-1})	6.99	8.18	8.19	9.49	10.7	10.6	12.1
[SCd] / [Cd_{Diss}]	10.2	9.53	9.20	9.31	9.00	8.80	9.20
K* (ml g^{-1})	714	662	643	652	629	612	648

Note: a. Student's t-test 95% error on analytically determined concentration.

Appendix 10·7 (section 10·3·2)

Parameters relating to the adsorption of 10.0–230 μgCd l^{-1} solution on silica sand at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 237	14 243	14 346	14 274	14 246	14 320
Equilibrium Cd concn (μg l^{-1})	9.65	9.90	28.8	28.8	52.0	48.3
Error[a] (μg l^{-1})	±0.4	±0.4	±1.3	±0.3	±4.5	±1.8
% Adsn	3.5	1.0	4.0	4.0	0	4.0
Adsn density (Γ_{Cd}) (μg g^{-1})	0.025	0.007	0.084	0.084	0	0.140
[SCd] / [Cd_{Diss}]	0.036	0.010	0.042	0.042	0	0.042
K* (ml g^{-1})	2.6	0.7	2.9	2.9	0	2.9

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] (mg l^{-1})	14 300	14 329	14 291	14 349	14 277	14 240
Equilibrium Cd concn (μg l^{-1})	70.2	70.1	92.6	90.0	106	110
Error[a] (μg l^{-1})	±.35	±2.2	±1.2	±3.3	±3	±4
% Adsn	0	0	(–2.2)	0	3.6	0
Adsn density (Γ_{Cd}) (μg g^{-1})	0	0	(–0.140)	0	0.280	0
[SCd] / [Cd_{Diss}]	0	0	(–0.022)	0	0.037	0
K* (ml g^{-1})	0	0	(–1.5)	0	2.6	0

Appendix 10·7 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[$Solid_T$] ($mg\ l^{-1}$)	14 249	14 297	14 314	14 311	14 263	14 246
Equilibrium Cd concn ($\mu g\ l^{-1}$)	140	134	148	155	192	180
Error[a] ($\mu g\ l^{-1}$)	±4	±4	±8	±9	±18	±14
% Adsn	(–7.7)	(–3.1)	1.3	(–3.3)	(–12.9)	(–5.9)
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	(–0.702)	(–0.003)	0.140	(–0.349)	(–1.54)	(–0.702)
[SCd] / [Cd_{Diss}]	(–0.072)	(–0.030)	(0.013)	(–0.032)	(–0.114)	(–0.056)
K* ($ml\ g^{-1}$)	(–5.0)	(–2.1)	0.9	(–2.3)	(–8.0)	(–3.9)

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[$Solid_T$] ($mg\ l^{-1}$)	14 366	14 360	14 263	14 343	14 294	14 294
Equilibrium Cd concn ($\mu g\ l^{-1}$)	180	188	208	210	230	240
Error[a] ($\mu g\ l^{-1}$)	±2	±3	±2	±10	±15	±8
% Adsn	5.3	10.5	1.0	0	0	(–4.3)
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	0.696	0.139	0.140	0	0	(–0.699)
[SCd] / [Cd_{Diss}]	0.056	0.117	0.010	0	0	(–0.041)
K* ($ml\ g^{-1}$)	3.9	8.2	0.7	0	0	(–2.9)

Note: **a.** Student's t-test 95% error on analytically determined concentration.

Appendix 10·8 (section 10·3·2)

Parameters relating to the adsorption (at pH 5.70 and 25 °C) of 10.0–230 μgCd l^{-1} solution on Tai Tapu silt loam with organic matter removed. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 257	14 257	14 229	14 240	14 217	14 254
Equilibrium Cd concn (μg l^{-1})	6.1	5.8	17.1	17.9	32.2	29.6
Error[a] (μg l^{-1})	±0.2	±0.2	±0.4	±0.7	±0.7	±0.2
% Adsn	39.0	42.0	43.0	40.3	35.6	40.8
Adsn density (Γ_{Cd}) (μg g^{-1})	0.274	0.295	0.907	0.850	1.25	1.43
[SCd] / [Cd_{Diss}]	0.639	0.724	0.754	0.675	0.553	0.689
K* (ml g^{-1})	44.8	50.8	53.0	47.4	38.9	48.4

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] (mg l^{-1})	14 220	14 246	14 271	14 303	14 211	14 337
Equilibrium Cd concn (μg l^{-1})	45.2	48.2	60.2	60.0	69.6	67.4
Error[a] (μg l^{-1})	±0.5	±0.8	±0.7	±2.2	±2.4	±0.2
% Adsn	35.4	31.1	33.1	33.3	36.7	38.7
Adsn density (Γ_{Cd}) (μg g^{-1})	1.74	1.53	2.09	2.10	2.84	2.97
[SCd] / [Cd_{Diss}]	0.548	0.451	0.495	0.499	0.580	0.631
K* (ml g^{-1})	38.5	31.7	34.7	34.9	40.8	44.0

Appendix 10·8 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 289	14 306	14 323	14 306	14 306	14 314
Equilibrium Cd concn ($\mu g\ l^{-1}$)	76.0	76.0	90.1	94.4	108	104
Error[a] ($\mu g\ l^{-1}$)	±1.0	±2.6	±1.0	±1.8	±2	±3
% Adsn	41.5	41.5	40.0	37.1	36.4	39.1
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	3.78	3.78	4.19	3.89	4.33	4.65
[SCd] / [Cd$_{Diss}$]	0.709	0.709	0.666	0.590	0.572	0.642
K* ($ml\ g^{-1}$)	49.6	49.6	46.5	41.2	40.0	44.9

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 263	14 249	14 246	14 246	14 240	14 326
Equilibrium Cd concn ($\mu g\ l^{-1}$)	130	129	130	139	142	144
Error[a] ($\mu g\ l^{-1}$)						
% Adsn	31.6	32.4	38.1	33.8	38.3	37.3
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	4.21	4.32	5.62	4.98	6.18	6.00
[SCd] / [Cd$_{Diss}$]	0.462	0.479	0.616	0.511	0.621	0.595
K* ($ml\ g^{-1}$)	32.4	33.6	43.2	35.8	43.6	41.5

Note: **a**. Student's t-test 95% error on analytically determined concentration.

Appendix 10·9 (section 10·3·2)

Parameters relating to the adsorption (at pH 5.70 and 25 °C) of 10.0–230 μgCd l^{-1} solution on Tai Tapu silt loam with iron and manganese oxides removed. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 274	14 257	14 320	14 300	14 223	14 257
Equilibrium Cd concn (μg l^{-1})	2.2	1.5	5.7	6.2	10.5	10.8
Error[a] (μg l^{-1})	±0.8	±0.8	±0.7	±0.5	±0.2	±0.6
% Adsn	78.5	85.0	81.2	79.5	79.0	78.5
Adsn density (Γ_{Cd}) (μg g^{-1})	0.550	0.596	1.70	1.67	2.78	2.75
[SCd] / [Cd_{Diss}]	3.65	5.67	4.32	3.88	3.76	3.65
K* (ml g^{-1})	256	397	302	271	264	256

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] (mg l^{-1})	14 240	14 231	14 317	14 291	14 317	14 217
Equilibrium Cd concn (μg l^{-1})	14.2	14.5	15.8	16.0	20.1	19.2
Error[a] (μg l^{-1})	±0.5	±0.2	±2.7	±2.1	±1.2	±1.4
% Adsn	79.7	79.4	82.4	82.2	81.7	82.5
Adsn density (Γ_{Cd}) (μg g^{-1})	3.92	3.90	5.18	5.18	6.28	6.39
[SCd] / [Cd_{Diss}]	3.93	3.85	4.68	4.62	4.46	4.71
K* (ml g^{-1})	276	271	327	323	312	332

Appendix 10·9 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 400	14 334	14 203	14 229	14 309	14 351
Equilibrium Cd concn ($\mu g\ l^{-1}$)	26.6	25.2	31.6	29.8	37.6	33.6
Error[a] ($\mu g\ l^{-1}$)	±0.9	±0.2	±1.6	±0.6	±2.3	±0.8
% Adsn	79.5	80.6	78.9	80.1	77.9	80.2
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	7.21	7.31	8.34	8.45	9.25	9.50
[SCd] / [Cd$_{Diss}$]	3.88	4.16	3.74	4.03	3.53	4.05
K* ($ml\ g^{-1}$)	269	290	263	283	246	282

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 297	14 223	14 220	14 257	14 266	14 277
Equilibrium Cd concn ($\mu g\ l^{-1}$)	37.2	36.0	39.6	39.6	46.0	46.8
Error[a] ($\mu g\ l^{-1}$)	±0.7	±0.6	±0.8	±0.8	±1.2	±0.4
% Adsn	80.4	81.1	81.1	81.1	80.0	79.7
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	10.7	10.8	12.0	12.0	12.9	12.8
[SCd] / [Cd$_{Diss}$]	4.10	4.29	4.29	4.29	4.00	3.92
K* ($ml\ g^{-1}$)	287	302	302	301	280	275

Note: **a.** Student's t-test 95% error on analytically determined concentration.

Appendix 10·10 (section 10·3·2)

Confidence intervals (95%) for the slopes and intercepts of the least-squares lines of the simple isotherms relating to adsorption of cadmium on whole soil and its components at pH 5.70 and 25 °C. (The original least-squares equations are given in Table 10·4.)

Substrate	Slope (g ml^{-1})		Intercept (μg g^{-1})	
	Lower limit	Upper limit	Lower limit	Upper limit
Whole soil	642	852	–3.83	–0.99
Sand fraction	183	406	–2.98	2.35
Silt fraction	281	363	–1.42	0.46
Clay fraction	517	631	0.71	1.70
Soil–org matter	35	43	–0.19	0.48
Soil–Fe & Mn oxides	263	297	–0.25	0.55

Appendix 10·11 (section 10·3·3)

Parameters relating to the adsorption of 10.0–230 μgCd l^{-1} solution on Tai Tapu silt loam at pH 7.00 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 386	14 429	14 206	14 226	14 366	14 249
Equilibrium Cd concn (μg l^{-1})	0.8	0.8	2.2	2.2	3.6	3.5
Error[a] (μg l^{-1})	±0.2	±0.2	±0.2	±0.2	±0.2	±0.1
% Adsn	91.8	91.6	92.6	92.7	92.8	93.0
Adsn density (Γ_{Cd}) (μg g^{-1})	0.638	0.635	1.96	1.95	3.23	3.26
[SCd] / [Cd_{Diss}]	11.2	10.9	12.5	12.7	12.9	13.3
K* (ml g^{-1})	778	756	881	893	897	932

Appendix 10·11 continued...

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn ($\mu g\ l^{-1}$)	70.0	70.0	90.0	90.0	110	110
[Solid$_T$] ($mg\ l^{-1}$)	14 266	14 294	14 291	14 229	14 257	14 257
Equilibrium Cd concn ($\mu g\ l^{-1}$)	5.0	4.9	8.7	8.6	8.2	7.9
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.2	±0.4	±0.5	±0.2	±0.7
% Adsn	92.9	93.0	90.3	90.4	92.5	92.8
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	4.56	4.55	5.69	5.72	7.14	7.16
[SCd] / [Cd$_{Diss}$]	13.1	13.3	9.31	9.42	12.3	12.9
K* ($ml\ g^{-1}$)	917	929	651	662	865	904

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 206	14 246	14 217	14 314	14 371	14 249
Equilibrium Cd concn ($\mu g\ l^{-1}$)	9.4	10.6	11.5	12.7	13.2	13.2
Error[a] ($\mu g\ l^{-1}$)	±0.3	±0.5	±0.2	±0.2	±0.8	±0.2
% Adsn	92.8	91.8	92.3	91.5	92.2	92.2
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	8.49	8.38	9.74	9.59	10.9	11.0
[SCd] / [Cd$_{Diss}$]	12.9	11.2	12.0	10.8	11.8	11.8
K* ($ml\ g^{-1}$)	907	786	843	752	823	830

Appendix 10·11 continued...

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 223	14 266	14 334	14 257	14 251	14 157
Equilibrium Cd concn ($\mu g\ l^{-1}$)	14.2	14.2	15.9	16.3	19.0	16.0
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.2	±0.2	±0.2	±2.2	±0.8
% Adsn	92.5	92.5	92.4	92.2	91.7	93.0
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	12.4	12.3	13.5	13.6	14.8	15.1
[SCd] / [Cd$_{Diss}$]	12.3	12.3	12.2	11.8	11.0	13.3
K* ($ml\ g^{-1}$)	867	865	848	829	775	938

Note: **a.** Student's t-test 95% error on analytically determined concentration.

Appendix 10·12 (section 10·3·3)

Parameters relating to the adsorption of 10.0–230 $\mu g Cd\ l^{-1}$ solution on Tai Tapu silt loam at pH 8.00 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn ($\mu g\ l^{-1}$)	10.0	10.0	30.0	30.0	50.0	50.0
[Solid$_T$] ($mg\ l^{-1}$)	14 220	14 220	14 217	14 294	14 323	14 363
Equilibrium Cd concn ($\mu g\ l^{-1}$)	0.9	1.0	1.9	2.2	4.1	3.4
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.2	±0.2	±0.2	±0.2	±0.3
% Adsn	90.6	89.8	93.7	92.6	91.8	93.2
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	0.637	0.632	1.98	1.94	3.21	3.24
[SCd] / [Cd$_{Diss}$]	9.64	8.80	14.9	12.5	11.2	13.7
K* ($ml\ g^{-1}$)	678	619	1 050	875	782	954

Appendix 10·12 continued...

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn ($\mu g\ l^{-1}$)	70.0	70.0	90.0	90.0	110	110
[Solid$_T$] ($mg\ l^{-1}$)	14 234	14 266	14 386	14 409	14 257	14 371
Equilibrium Cd concn ($\mu g\ l^{-1}$)	4.4	4.4	5.1	5.3	6.2	6.4
Error[a] ($\mu g\ l^{-1}$)	±0.4	±0.2	±0.1	±0.6	±0.5	±0.6
% Adsn	93.7	93.7	94.3	94.1	94.4	94.2
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	4.61	4.60	5.90	5.88	7.28	7.21
[SCd] / [Cd$_{Diss}$]	14.9	14.9	16.5	15.9	16.9	16.2
K* ($ml\ g^{-1}$)	1 040	1 040	1 150	1 110	1 180	1 130

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 289	14 266	14 277	14 286	14 380	14 403
Equilibrium Cd concn ($\mu g\ l^{-1}$)	9.0	8.7	11.6	10.9	11.9	10.9
Error[a] ($\mu g\ l^{-1}$)	±0.5	±0.5	±0.4	±0.5	±1.0	±1.4
% Adsn	93.1	93.3	92.3	92.7	93.0	93.6
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	8.47	8.50	9.69	9.74	11.0	11.0
[SCd] / [Cd$_{Diss}$]	13.5	13.9	12.0	12.7	13.3	14.3
K* ($ml\ g^{-1}$)	944	976	840	889	924	1 020

Appendix 10·12 continued...

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 223	14 242	14 229	14 203	14 269	14 317
Equilibrium Cd concn ($\mu g\ l^{-1}$)	13.2	10.9	14.4	15.0	18.4	17.4
Error[a] ($\mu g\ l^{-1}$)	±0.5	±0.5	±1.0	±0.3	±0.4	±0.4
% Adsn	93.1	94.3	93.1	91.2	92.0	92.4
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	12.4	12.6	13.7	13.5	14.8	14.8
[SCd] / [Cd$_{Diss}$]	13.5	16.5	13.5	10.4	11.5	12.2
K* ($ml\ g^{-1}$)	949	1 160	948	730	806	849

Note: **a.** Student's t-test 95% error on analytically determined concentration.

Appendix 10·13 (section 10·3·3)

Confidence intervals (95%) for the slopes and intercepts of the least-squares lines of the simple isotherms relating to adsorption of cadmium on whole soil at pH 5.70, pH 7.00 and pH 8.00. (The original least-squares equations are given in Table 10·6.)

	Slope ($g\ ml^{-1}$)		Intercept ($\mu g\ g^{-1}$)	
	Lower limit	Upper limit	Lower limit	Upper limit
Simple regression				
pH 5.70	642	852	–3.83	–0.99
pH 7.00	772	889	–0.48	0.60
pH 8.00	785	942	0.05	1.34
Freundlich model least-squares line				
pH 5.70	1.00	1.37	6.27	7.87
pH 7.00	0.95	1.05	6.49	6.97
pH 8.00	0.98	1.14	6.75	7.56

Appendix 10·14 (section 10·3·4)

Parameters relating to the competitive adsorption of Cd^{2+} and Zn^{2+} from solutions containing 40.0 μgZn ml^{-1} and 10.0–230 μgCd l^{-1} onto Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn (μg l^{-1})	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] (mg l^{-1})	14 209	14 263	14 394	14 343	14 240	14 297
Equilibrium Cd concn (μg l^{-1})	4.4	5.1	10.5	10.9	17.8	17.2
Error[a] (μg l^{-1})	±0.4	±0.4	±0.3	±0.2	±0.2	±0.2
% Adsn	56.0	49.0	65.0	63.7	64.4	65.6
Adsn density (Γ_{Cd}) (μg g^{-1})	0.394	0.344	1.36	1.33	2.26	2.29
[SCd] / [Cd_{Diss}]	1.27	0.961	1.86	1.76	1.81	1.91
K* (ml g^{-1})	89.6	67.4	129	122	127	133

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn (μg l^{-1})	70.0	70.0	90.0	90.0	110	110
[$Solid_T$] (mg l^{-1})	14 323	14 291	14 234	14 383	14 351	14 277
Equilibrium Cd concn (μg l^{-1})	26.4	27.1	39.8	38.2	47.2	47.6
Error[a] (μg l^{-1})	±0.3	±1.0	±1.2	±2.6	±1.9	±2.0
% Adsn	62.3	61.3	55.8	57.6	57.1	56.7
Adsn density (Γ_{Cd}) (μg g^{-1})	3.04	3.00	3.53	3.60	4.37	4.37
[SCd] / [Cd_{Diss}]	1.65	1.58	1.26	1.36	1.33	1.31
K* (ml g^{-1})	115	111	88.7	94.4	92.7	91.7

Appendix 10·14 continued...

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 269	14 294	14 203	14 340	14 271	14 291
Equilibrium Cd concn ($\mu g\ l^{-1}$)	48.8	52.4	59.6	59.2	61.6	62.4
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.7	±0.6	±2.8	±2.2	±0.3
% Adsn	62.5	61.3	55.8	57.6	57.7	56.7
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	5.69	5.43	6.37	6.33	7.60	7.53
[SCd] / [Cd$_{Diss}$]	1.67	1.48	1.52	1.53	1.76	1.73
K* ($ml\ g^{-1}$)	117	104	107	107	123	121

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 300	14 249	14 186	14 300	14 214	14 260
Equilibrium Cd concn ($\mu g\ l^{-1}$)	69.6	69.8	71.6	76.0	75.2	75.2
Error[a] ($\mu g\ l^{-1}$)	±1.6	±2.5	±3.5	±0.5	±1.0	±1.5
% Adsn	63.4	63.3	65.9	63.8	67.3	67.3
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	8.42	8.44	9.76	9.37	10.9	10.9
[SCd] / [Cd$_{Diss}$]	1.73	1.73	1.93	1.76	2.06	2.06
K* ($ml\ g^{-1}$)	121	121	136	123	145	145

Appendix 10·14 continued...

Parameter	Sample number					
	1	2	3	4	5	6
Initial Zn concn ($\mu g\ ml^{-1}$)	40.0	40.0	40.0	40.0	40.0	40.0
Equilibrium Zn concn ($\mu g\ ml^{-1}$)	23.6	24.8	24.0	24.3	23.6	23.2
%Zn Adsn	41.0	38.0	40.0	39.3	41.0	42.0
Adsn density (Γ_{Zn}) ($\mu g\ g^{-1}$)	1 150	1 070	1 112	1 090	1 150	1 180
$[SZn] / [Zn_{Diss}]$	0.695	0.613	0.667	0.647	0.695	0.724
K* ($ml\ g^{-1}$)	48.9	43.0	46.3	45.1	48.8	50.6

Parameter	Sample number					
	7	8	9	10	11	12
Initial Zn concn ($\mu g\ ml^{-1}$)	40.0	40.0	40.0	40.0	40.0	40.0
Equilibrium Zn concn ($\mu g\ ml^{-1}$)	24.0	24.0	23.2	23.6	24.0	22.4
%Zn Adsn	40.0	40.0	42.0	41.0	40.0	44.0
Adsn density (Γ_{Zn}) ($\mu g\ g^{-1}$)	1 120	1 120	1 180	1 140	1 120	1 230
$[SZn] / [Zn_{Diss}]$	0.667	0.667	0.724	0.695	0.667	0.786
K* ($ml\ g^{-1}$)	45.6	46.7	50.9	48.3	46.5	55.0

Parameter	Sample number					
	13	14	15	16	17	18
Initial Zn concn ($\mu g\ ml^{-1}$)	40.0	40.0	40.0	40.0	40.0	40.0
Equilibrium Zn concn ($\mu g\ ml^{-1}$)	22.4	23.0	23.3	22.4	22.0	21.6
%Zn Adsn	44.0	42.5	41.8	44.0	45.0	46.0
Adsn density (Γ_{Zn}) ($\mu g\ g^{-1}$)	1 230	1 190	1 180	1 230	1 260	1 290
$[SZn] / [Zn_{Diss}]$	0.786	0.739	0.718	0.786	0.818	0.852
K* ($ml\ g^{-1}$)	55.1	51.7	50.6	54.8	57.3	59.6

Appendix 10·14 continued...

Parameter	Sample number					
	19	20	21	22	23	24
Initial Zn concn ($\mu g\ ml^{-1}$)	40.0	40.0	40.0	40.0	40.0	40.0
Equilibrium Zn concn ($\mu g\ ml^{-1}$)	22.0	22.6	23.0	20.6	22.7	22.4
%Zn Adsn	45.0	43.5	42.5	48.5	43.3	44.0
Adsn density (G_{Zn}) ($\mu g\ g^{-1}$)	1 260	1 220	1 200	1 360	1 220	1 230
[SZn] / [Zn_{Diss}]	0.818	0.770	0.739	0.942	0.764	0.786
K* ($ml\ g^{-1}$)	57.2	54.0	52.1	65.9	53.8	55.1

Note: **a**. Student's t-test 95% error on analytically determined concentration.

Appendix 10·15 (section 10·3·4)

Parameters relating to the competitive adsorption of Cd^{2+} and Pb^{2+} from solutions containing 3.00 µgPb ml^{-1} and 10.0–230 µgCd l^{-1} onto Tai Tapu silt loam at pH 5.70 and 25 °C. (Terms are defined in section 10·1·2.)

Parameter	Sample number					
	1	2	3	4	5	6
Initial Cd concn ($\mu g\ l^{-1}$)	10.0	10.0	30.0	30.0	50.0	50.0
[$Solid_T$] ($mg\ l^{-1}$)	14 389	14 254	14 266	14 403	14 329	14 346
Equilibrium Cd concn ($\mu g\ l^{-1}$)	2.1	2.2	7.0	6.7	13.0	13.0
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.2	±0.2	±0.2	±0.2	±0.2
% Adsn	79.5	78.5	76.8	77.7	74.0	74.0
Adsn density (G_{Cd}) ($\mu g\ g^{-1}$)	0.553	0.551	1.62	1.62	2.58	2.58
[SCd] / [Cd_{Diss}]	3.88	3.65	3.31	3.48	2.85	2.85
K* ($ml\ g^{-1}$)	270	256	232	242	199	198

Appendix 10·15 continued...

Parameter	Sample number					
	7	8	9	10	11	12
Initial Cd concn ($\mu g\ l^{-1}$)	70.0	70.0	90.0	90.0	110	110
[Solid$_T$] ($mg\ l^{-1}$)	14 331	14 271	14 254	14 231	14 203	14 211
Equilibrium Cd concn ($\mu g\ l^{-1}$)	12.4	12.4	15.2	15.0	1.4	18.0
Error[a] ($\mu g\ l^{-1}$)	±0.6	±0.6	±0.5	±0.4	±0.3	±1.2
% Adsn	82.3	82.3	83.1	83.3	83.3	83.6
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	4.02	4.04	5.25	5.27	6.45	6.47
[SCd] / [Cd$_{Diss}$]	4.65	4.65	4.92	4.99	4.99	5.10
K* ($ml\ g^{-1}$)	324	326	345	351	351	359

Parameter	Sample number					
	13	14	15	16	17	18
Initial Cd concn ($\mu g\ l^{-1}$)	130	130	150	150	170	170
[Solid$_T$] ($mg\ l^{-1}$)	14 203	14 326	14 334	14 363	14 206	14 260
Equilibrium Cd concn ($\mu g\ l^{-1}$)	24.0	23.0	26.8	27.8	34.6	34.6
Error[a] ($\mu g\ l^{-1}$)	±2.9	±0.2	±0.8	±0.4	±0.2	±0.4
% Adsn	81.5	82.3	82.1	81.5	79.6	79.6
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	7.46	7.47	8.60	8.51	9.53	9.49
[SCd] / [Cd$_{Diss}$]	4.41	4.65	4.59	4.41	3.90	3.90
K* ($ml\ g^{-1}$)	310	325	320	307	275	274

Appendix 10·15 continued...

Parameter	Sample number					
	19	20	21	22	23	24
Initial Cd concn ($\mu g\ l^{-1}$)	190	190	210	210	230	230
[Solid$_T$] ($mg\ l^{-1}$)	14 303	14 309	14 309	14 171	14 234	14 194
Equilibrium Cd concn ($\mu g\ l^{-1}$)	35.2	35.2	34.0	37.6	43.2	41.4
Error[a] ($\mu g\ l^{-1}$)	±0.2	±0.3	±0.3	±0.3	±0.9	±0.8
% Adsn	81.5	81.5	83.8	82.1	81.2	82.0
Adsn density (Γ_{Cd}) ($\mu g\ g^{-1}$)	10.8	10.8	12.3	12.2	13.1	13.3
[SCd] / [Cd$_{Diss}$]	4.41	4.41	5.17	4.59	4.32	4.56
K* ($ml\ g^{-1}$)	308	308	362	324	303	321

Parameter	Sample number					
	1	2	3	4	5	6
Initial Pb concn ($\mu g\ ml^{-1}$)	3.00	3.00	3.00	3.00	3.00	3.00
Equilibrium Pb concn ($\mu g\ ml^{-1}$)	0.20	0.18	0.18	0.20	0.20	0.18
%Pb Adsn	93.3	94.2	94.2	93.3	93.3	94.2
Adsn density (Γ_{Pb}) ($\mu g\ g^{-1}$)	195	198	198	194	197	197
[SPb] / [Pb$_{Diss}$]	13.9	16.2	16.2	13.9	13.9	16.2
K* ($ml\ g^{-1}$)	968	1 140	1 140	967	972	1 130

Appendix 10·15 continued...

Parameter	Sample number					
	7	8	9	10	11	12
Initial Pb concn ($\mu g\ ml^{-1}$)	3.00	3.00	3.00	3.00	3.00	3.00
Equilibrium Pb concn ($\mu g\ ml^{-1}$)	0.20	0.18	0.18	0.18	0.18	0.18
%Pb Adsn	93.3	94.2	94.2	94.2	94.2	94.2
Adsn density (Γ_{Pb}) ($\mu g\ g^{-1}$)	195	198	198	198	199	199
[SPb] / [Pb_{Diss}]	13.9	16.2	16.2	16.2	16.2	16.2
K* ($ml\ g^{-1}$)	972	1 140	1 140	1 140	1 140	1 140

Parameter	Sample number					
	13	14	15	16	17	18
Initial Pb concn ($\mu g\ ml^{-1}$)	3.00	3.00	3.00	3.00	3.00	3.00
Equilibrium Pb concn ($\mu g\ ml^{-1}$)	0.20	0.20	0.18	0.20	0.18	0.18
%Pb Adsn	93.3	93.3	94.2	93.3	94.2	94.2
Adsn density (Γ_{Pb}) ($\mu g\ g^{-1}$)	197	195	197	195	199	198
[SPb] / [Pb_{Diss}]	13.9	13.9	16.2	13.9	16.2	16.2
K* ($ml\ g^{-1}$)	980	972	1 130	971	1 140	1 140

Parameter	Sample number					
	19	20	21	22	23	24
Initial Pb concn ($\mu g\ ml^{-1}$)	3.00	3.00	3.00	3.00	3.00	3.00
Equilibrium Pb concn ($\mu g\ ml^{-1}$)	0.20	0.18	0.18	0.20	0.18	0.18
%Pb Adsn	93.3	94.2	94.2	93.3	94.2	94.2
Adsn density (Γ_{Pb}) ($\mu g\ g^{-1}$)	196	197	197	198	198	199
[SPb] / [Pb_{Diss}]	13.9	16.2	16.2	13.9	16.2	16.2
K* ($ml\ g^{-1}$)	974	1 140	1 140	983	1 140	1 140

Note: **a.** Student's t-test 95% error on analytically determined concentration.

Appendix 10·16 (section 10·3·4)

Confidence intervals (95%) for the slopes and intercepts of the least-squares lines of the simple isotherms relating to adsorption of cadmium on whole soil in the presence of lead and zinc. (The original least-squares equations are given in Table 10·9.)

	Slope (g ml^{-1})		Intercept (μg g^{-1})	
	Lower limit	Upper limit	Lower limit	Upper limit
Simple regression				
no competition	642	852	–3.83	–0.99
with 40 μgZn ml^{-1}	116	145	–1.21	0.09
with 3 μgPb ml^{-1}	291	344	–0.78	0.40
Freundlich model least-squares line				
no competition	1.00	1.37	6.27	7.87
with 40 μgZn ml^{-1}	1.01	1.18	4.74	5.31
with 3 μgPb ml^{-1}	1.00	1.17	5.70	6.37

CHAPTER 11
THE MOBILITY OF CADMIUM IN A CHRISTCHURCH SOIL

11·1 Introduction

The mobility of metals in soils is dependent on a number of factors, including the annual amount of water infiltration, the concentrations of the metals' mobile species, and the sorption characteristics, bulk density and porosity of the soil (Baes and Sharp, 1983; Brown *et al.* 1983; Ram and Verloo, 1985; Trefry and Metz, 1984). The prime mobile species of cadmium in soils is the divalent ion (Cd^{2+}) (Hermann and Neumann-Mahlkau, 1985).

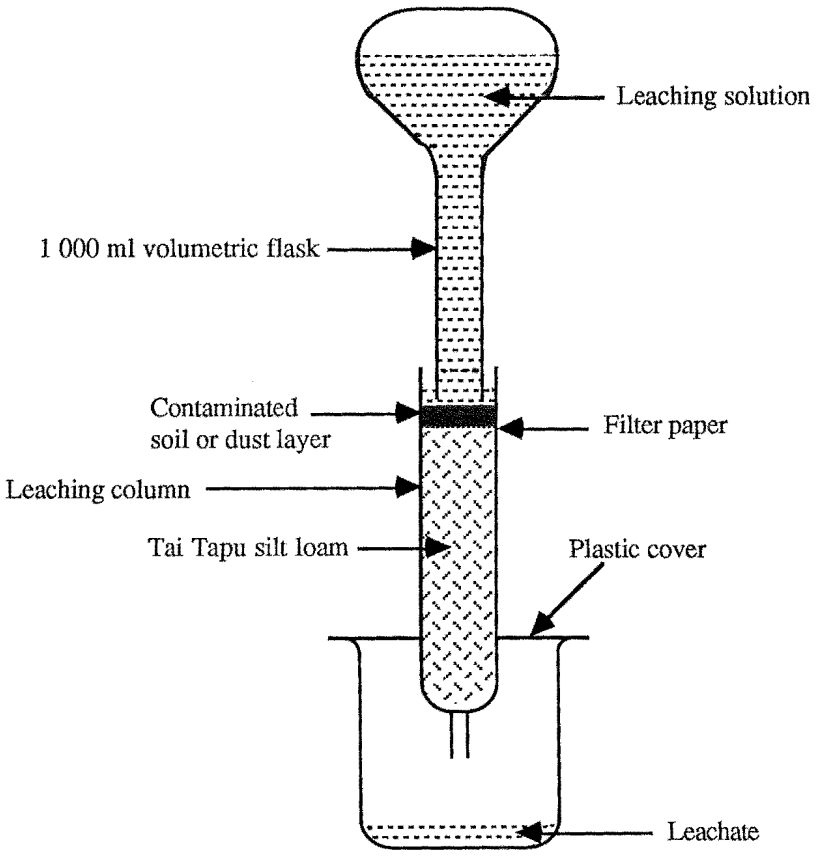
It was concluded in Chapter 10 that Tai Tapu silt loam has a high affinity for trace amounts of cadmium, a finding which suggested that cadmium's mobility in this soil would be limited. In this study, the mobility of cadmium in Tai Tapu silt loam, and some of the factors which influence it, were examined more directly. For purposes of comparison, copper, lead and zinc mobility measurements were also made in some cases.

11·2 Method

A schematic diagram of the apparatus used in all the leaching experiments is presented in Figure 11·1.

Figure 11·1

Schematic diagram of the apparatus used in the cadmium leaching experiments.



All experiments in this study were carried out using the same batch of Tai Tapu silt loam that was collected and used for the cadmium adsorption experiments (section 10·2·1). Mean levels of cadmium, copper, lead and zinc found in this sample, and their 95% confidence intervals, are given in Appendix 11·1.

Glass columns of 24 mm internal diameter were bisected lengthwise and rejoined with a waterproof glue ("Silaflex RTV"). Prior to being rejoined, the sides of the columns were soaked in 4M AR nitric acid for 48 hr and thoroughly rinsed with double-distilled water. A tapered end-piece (also acid-washed) was glued to the bottom of each column, and a small circle of (acid washed and double-distilled water rinsed) filter paper was placed over the internal mouth of the end-piece. Each column was then packed with 10 cm (or in some cases 20 cm) of the processed Tai Tapu silt loam; processing of this sample is detailed in section 10·2·1. A filter paper of diameter 22 mm (acid washed and double-distilled water rinsed) was placed on the soil's surface, and about 0.8 g of cadmium-contaminated material was distributed evenly over the filter paper. Leaching solutions, held in inverted 1 000 ml volumetric flasks, were then allowed to pass through the columns.

Leaching of cadmium was investigated from the following cadmium-contaminated materials:

1. A sample of the dust collected from near an electroplating firm ("electroplating firm # 1", mentioned in section 3·3·2b). This sample was found to contain (36.8 ± 1.8) μgCd g^{-1}, (20 000 ± 1 100) μgCu g^{-1}, (7 420 ± 120) μgPb g^{-1} and (7 900 ± 420) μgZn g^{-1}. As it was the only dust sample used, this sample will be referred to hereafter as the *contaminated dust sample.*
2. A sample of Tai Tapu silt loam spiked with cadmium from a 10 mgCd ml^{-1} standard solution, prepared from cadmium sulphate ($3CdSO_4.8H_2O$). After drying, the total cadmium content of this material was (37.00 ± 0.01) μgCd g^{-1}.
3. Samples of solid cadmium carbonate, solid cadmium oxide and solid cadmium sulphide diluted with silica sand (mentioned in sections 10·2·1 and 10·3·2) to total cadmium concentrations (in all cases) of (37.00 ± 0.01) μgCd g^{-1}.

An estimate of the mobility of cadmium in Tai Tapu silt loam under conditions approximating those found in the environment was obtained by leaching duplicate 0.8 g portions of the contaminated dust sample with 1 155 ml of rainwater. It was calculated that in the leaching columns, this volume was equivalent to the mean annual rainfall experienced by Christchurch over the period 1983–1986 (638 mm yr^{-1}, Anon. 1987). Rainwater was collected for this purpose from the roof of the Rutherford Building, University of Canterbury, on various days during 1988. The pH of the (aggregate) rainwater sample was found by pH-meter to be 5.18. The concentrations of cadmium (measured by GFAAS) and copper, lead and zinc (measured by FAAS) in the rainwater were below analytical detection limits (< 0.2 μgCd l^{-1}, < 0.04 μgCu ml^{-1}, < 0.11 μgPb ml^{-1}, < 0.01 μgZn ml^{-1}).

The effect of pH on the mobility of cadmium, copper, lead and zinc in soil was assessed by leaching duplicate (about 0.8 g) portions of the contaminated dust sample and the sample of Tai Tapu silt loam spiked with cadmium from a standard solution with

1 155 ml of 0.01 M AR acetic acid/sodium acetate buffers of pH 3.00 and pH 4.70, and with 0.01 M AR potassium dihydrogen phosphate/disodium hydrogen phosphate buffers of pH 6.85. Leaching solution of the latter pH was also prepared in the form of an acetic acid/sodium acetate buffer and passed through a leaching column covered with a portion of the contaminated dust sample, in order to determine whether or not the low solubility of cadmium in solutions containing phosphate anions was hindering cadmium's mobility in Tai Tapu silt loam (Pickering, 1980).

All buffers were prepared in double-distilled water; sodium acetate/acetic acid buffers were constructed according to the method given in section 10·2·2, and the phosphate-containing buffer was prepared by addition of equal amounts of 0.01 M AR potassium dihydrogen phosphate solution (KH_2PO_4) and 0.01 M AR disodium hydrogen phosphate solution (Na_2HPO_4).

The effect of adding the leaching solutions intermittently was gauged by adding a (pH 4.70 0.01 M acetic acid/sodium acetate) leaching solution to two further soil columns (each covered with a layer of the contaminated dust sample) in 100 ml increments, and allowing time for drainage before subsequent additions of the leaching solution. A total volume 1 155 ml of the leaching solution was added to each of these columns, corresponding to the average annual rainfall. Four soil columns, each covered with a layer of the contaminated dust sample, were also leached with varying total amounts of this leaching solution, in order to gain some insight into the dynamics of the leaching process. Volumes of leaching solution added to the first, second, third and forth columns were 231 ml, 462 ml, 693 ml and 924 ml, respectively, corresponding to the equivalent of 20%, 40%, 60% and 80% (respectively) of the average annual rainfall.

The influence of cadmium's speciation on its mobility was also investigated: three soil columns, each covered with a silica sand-diluted solid form species of cadmium (cadmium carbonate, cadmium oxide, or cadmium sulphide) were leached with 1 155 ml of solution. In order to achieve a good separation, an acetic acid/sodium acetate buffer (0.01 M) of relatively high acidity (pH 3.00) was used as the leaching solution in this part of the study.

Leaching solutions corresponding in volume to the average annual rainfall generally took 3–4 weeks to pass through the soil columns. After this time, the columns were left to drain for 3–4 days, and then bisected along the glued lines. The soil in the columns was divided into 1 cm (depth) segments, which were oven dried, weighed, crushed and homogenized. The leached cadmium-contaminated soil, sand or dust layers were treated in the same manner. (In two cases, the extent of metal movement was also monitored by analysing the leachates.)

Soil samples were digested and prepared for analysis according to the methods given in section 3·2·2. Concentrations of copper, lead and zinc in digestion extracts were determined by FAAS, using the parameters given in Chapter 14, whereas cadmium concentrations were determined by GFAAS, using the parameters given in section 3·2·2. Amounts (μg) of cadmium, copper, lead and zinc calculated to be in the contaminated (dust,

sand or soil) layer and in each centimetre of the Tai Tapu silt loam at the beginning of each experiment were subtracted from the amounts determined after leaching.

The method of standard additions revealed that no significant (>4%) interferences were present in the GFAAS analysis of cadmium, or in the FAAS analyses of copper, lead or zinc. Estimates of the precision and bias of the analytical method were obtained by replicate analyses of a certified-reference sediment sample (SDN1/2; International Atomic Energy Agency, Vienna); this sample was included with many of the batches digested and analysed, and the results of these analyses are given in Table 11·1.

Table 11·1

Summary statistics relating to the repeated analyses certified-reference sediment (SDN1/2, IAEA Vienna).

	Cadmium	Copper	Lead	Zinc
Certified concn ($\mu g\ g^{-1}$)	11.0	72.2	120	439
This study:				
Number of analyses	15	11	11	11
Mean concn ($\mu g\ g^{-1}$)	10.6	70.9	116	405
Std deviation ($\mu g\ g^{-1}$)	1.2	1.7	19	13
95% error[a] on mean	±0.5	±1.0	±11	±7
Coeff of variation[b] (%)	11.3	2.4	16.4	3.2
Estimated recovery (%)	96.4	98.1	96.7	92.2

Notes: **a.** Student's t-test.
b. 100[standard deviation/mean].

The data in Table 11.1 were seen to indicate satisfactory levels of precision (mean coefficient of variation, 8%) and high recoveries (mean recovery, 96%) of cadmium, copper, lead and zinc in the analysis of the certified-reference sediment sample. However, errors in the actual mobility experiments were cumulative. For instance, the error on the estimated recovery of cadmium in a particular mobility experiment is the sum of the errors associated with the analytically determined amounts (μg) of cadmium in the contaminated layer before leaching, in the Tai Tapu silt loam before leaching, in the contaminated layer after leaching, and in the Tai Tapu silt loam after leaching; which, assuming an error of ±5% for each determination, would be about ±20%.

11·3 Results and discussion

11·3·1 Leaching of cadmium, copper, lead and zinc from the contaminated dust sample with rainwater

Results pertaining to the leaching of cadmium, copper, lead and zinc from the contaminated dust sample using 1 155 ml of rainwater (pH 5.18) as the leaching solution are listed in Table 11·2.

Table 11·2

Amounts and percentages of cadmium, copper, lead and zinc leached from the contaminated dust sample and incorporated into the soil column using 1 155 ml of rainwater as the leaching solution.

	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Column # 1								
Top layer								
Original amount	32.3	17 800	6 730	6 900	100	100	100	100
After leaching	24.9	17 400	6 100	5 310	–22.9	–2.2	–9.4	–22.7
Gained by soil								
0–1 cm	5.25	115	0	1 130	16.3	0.6	0	16.4
1–2 cm	0	0	0	0	0	0	0	0
Leachate[a]	<0.2	<46	<130	<12				
Recovery	30.2	17 520	6 100	6 440	93.4	98.4	90.6	93.3
Column # 2								
Top layer								
Original amount	31.2	17 100	6 480	6 950	100	100	100	100
After leaching	20.5	18 400	6 020	5 300	–34.3	7.6	–7.1	–23.7
Gained by soil								
0–1 cm	6.72	211	0	2 000	21.5	1.2	0	28.8
1–2 cm	0	0	0	0	0	0	0	0
Leachate[a]	<0.2	<46	<130	<12				
Recovery	27.2	18 600	6 020	7 300	87.2	109	92.9	106

Note: **a.** Concentrations of the four metals in the leachates were below detection limits.

Overall, leaching the contaminated dust sample with a volume of rainwater equivalent to one year's rainfall caused little movement of cadmium, copper, lead or zinc—either from the contaminated surface layers, or through the soil columns (Table 11·2). Additionally, levels of the four metals in the leachates remained below analytical detection limits (section 11·2). Recoveries of the four metals were better than expected, given the magnitude of the (cumulative) errors involved in their estimation (Table 11·2).

Mean losses from the contaminated surface layer were 29% for cadmium, 3% for copper, 8% for lead and 23% for zinc; mean gains by the 0–1 cm layer of the soil column were 19% for cadmium, 1% for copper, 0% for lead, and 23% for zinc. No additional lead was detected in the 0–1 cm layer, and no additional cadmium, copper, or zinc were detected in soil taken from greater depths than 1 cm.

In terms of cadmium, these findings suggest that in the short-to-medium term (1–5 years) the mobile fraction (presumably mainly Cd^{2+}) of a cadmium-containing substance applied to Tai Tapu silt loam is likely to remain within the soil's surface layers (0–5 cm). Thus, the mobile fraction of the cadmium applied to the soil surface is likely to be available to plant roots in the short-to-medium term, and is unlikely to leach to the ground-water (Kabata-Pendias and Pendias, 1985; section 10·1·1; Chapter 8). This conclusion is in agreement with that implied by the results of the experiment examining cadmium adsorption onto Tai Tapu silt loam at its natural pH (section 10·3·2).

The relative mobilities of the four metals in Tai Tapu silt loam under these conditions appear to follow the order cadmium ≈ zinc > copper ≈ lead (Table 11·2). This ranking of relative mobilities can be compared with the sequence quoted by Brown *et al.* (1985) for a large variety of soils: cadmium ≈ zinc > lead > copper. Brown *et al.* (1985) and Ram and Verloo (1985) have also reported similarities in the mobility patterns of the metal pairs cadmium and zinc, and copper and lead in soils.

Copper can be strongly complexed by soil organic matter (which comprises 12% of the Tai Tapu silt loam by weight), and the mobile species of lead (Pb^{2+}) is stable only at pH values of less than 2; factors which may account for the lack of movement shown by copper and lead (Brown *et al.* 1985; Hermann and Neumann-Mahlkau, 1985; Appendix 10·2).

It has been proposed by several authors that simple adsorption of cadmium onto organic matter is the predominant factor governing cadmium's mobility in soils (Brown *et al.* 1985; Jones and Symon, 1987; Ram and Verloo, 1985; Rothbaum *et al.* 1986). This could well be true in the case of Tai Tapu silt loam, given that (a) the organic content of Tai Tapu silt loam is relatively high, and (b) of all the adsorption experiments, destruction of the organic fraction caused the strongest reduction in the soil's overall ability to adsorb cadmium (section 10·3·2).

11·3·2 Effect of pH on the mobilities of cadmium, copper, lead and zinc in Tai Tapu silt loam

The results of all leaching experiments which involved the use of buffers of pH 6.85 are listed in Tables 11·3 and 11·4.

Soil depth-profiles of additional cadmium, copper, lead and zinc (μg) and surface layer losses of the four metals in columns through which 1 155 ml of pH 6.85 phosphate-containing buffer was passed are similar to depth-profiles and losses of the metals which occurred upon treatment of the columns with 1 155 ml of rainwater (Tables 11·2 and 11·3). No extra cadmium, copper, or zinc were detected in soil taken from greater depths than 1 cm.

Table 11·3

Results of the three leaching experiments in which the contaminated dust sample was leached with buffers of pH 6.85.

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
1 155 ml pH 6.85 phosphate buffer								
Column # 1								
Top layer:								
Original amount	29.4	16 100	6 110	6 300	100	100	100	100
After leaching	23.7	18 500	5 360	6 630	–19.4	+14.9	–12.3	+5.2
Gained by soil:								
0–1 cm	5.66	1 760	1 320	1 040	19.3	10.9	21.6	16.5
1–2 cm	0	0	0	0	0	0	0	0
Recovery (within column)	29.4	20 300	6 680	7 670	100	126	109	122
Column # 2								
Top layer:								
Original amount	29.4	16 100	6 110	6 300	100	100	100	100
After leaching	22.6	18 800	5 050	5 240	–23.1	+16.8	–17.3	–16.8
Gained by soil:								
0–1 cm	5.91	558	275	558	20.1	3.5	4.5	8.9
1–2 cm	0	0	0	0	0	0	0	0
Recovery (within column)	28.5	19 400	5 330	5 800	97.0	120	87.2	92.0
1 155 ml pH 6.85 acetate buffer								
Top layer:								
Original amount	29.6	16 200	6 020	6 340	100	100	100	100
After leaching	23.2	11 700	4 430	4 200	–21.6	–27.9	–26.4	–33.8
Gained by soil:								
0–1 cm	8.72	537	27.6	986	29.5	3.3	0.5	15.5
1–2 cm	0	0	0	0	0	0	0	0
Recovery (within column)	31.9	12 200	4 460	5 190	108	75.4	74.0	81.7

Table 11·4

Results of the two leaching experiments in which cadmium-spiked Tai Tapu silt loam was leached with leaching solutions of pH 6.85.

Leaching solution	Total µg cadmium		Percent of µgCd deposited	
	Column # 1	Column # 2	Column # 1	Column # 2
1 155 ml pH 6.85 phosphate buffer				
Top layer:				
Original amount	29.7	30.1	100	100
Amount after leaching	22.2	23.8	–25.4	–20.8
Gained by soil:				
0–1 cm	6.0	6.6	20.2	21.9
1–2 cm	0	0	0	0
Recovery (within column)	28.2	30.4	94.9	101

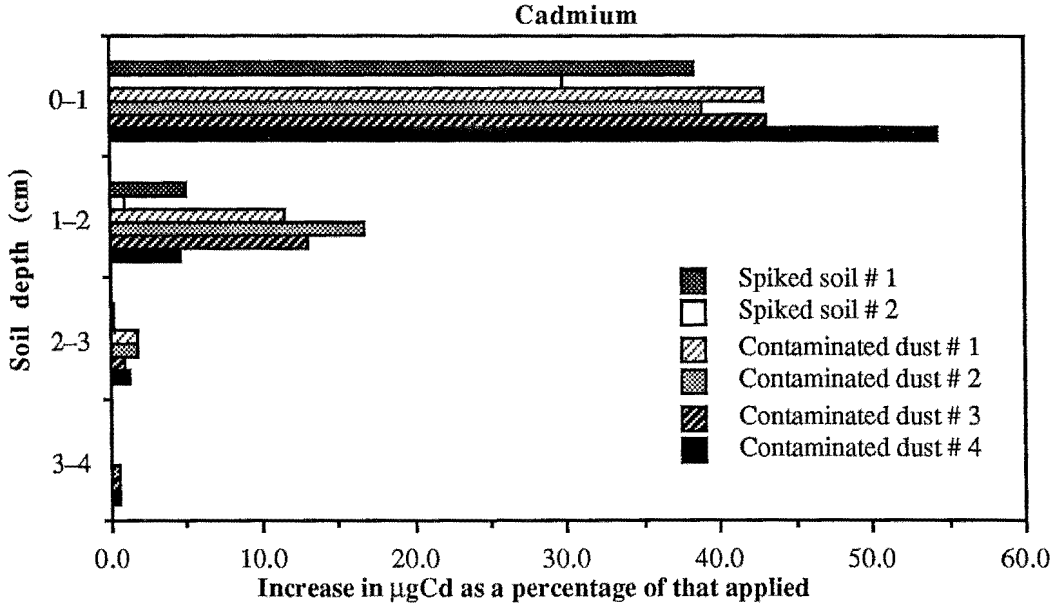
Substitution of the 0.01 M potassium dihydrogen phosphate/disodium hydrogen phosphate buffer with an acetic acid/sodium acetate buffer of the same pH caused no detectable difference in the depths to which the four metals leached (Table 11·3). However, the amount (µg) of cadmium in the 0–1 cm layer of the column treated with acetic acid/sodium acetate buffer appears to be slightly (≤1.5 times) higher than is the case for the other columns, suggesting that the low solubility of cadmium in solutions containing phosphate anions could have had a minor retarding effect on cadmium's mobility in Tai Tapu silt loam (Pickering, 1980).

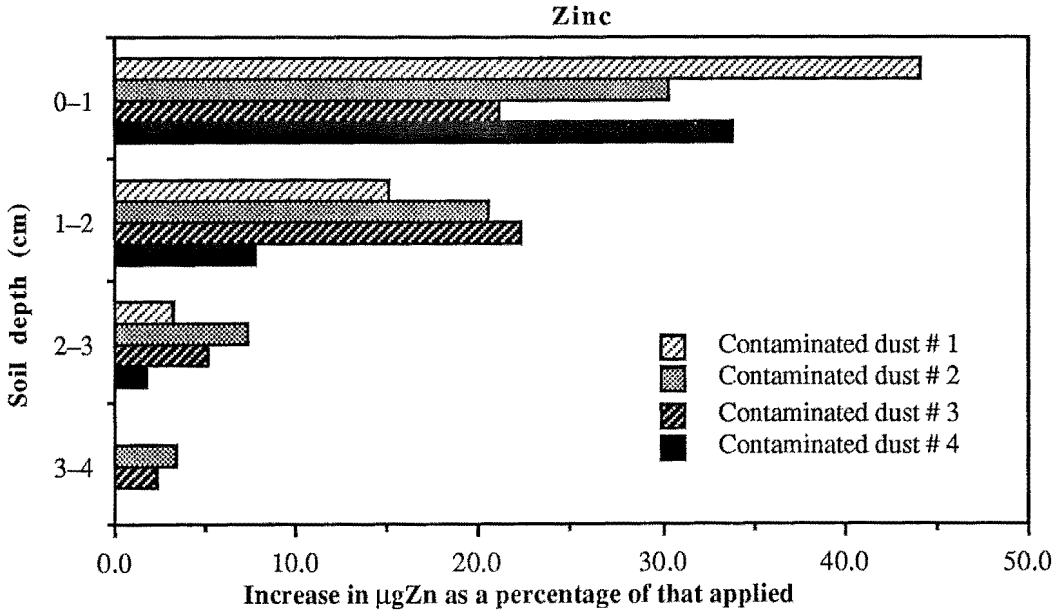
The cadmium depth-profile (µg) obtained at pH 6.85 using the cadmium-spiked Tai Tapu silt loam as the surface layer was more or less identical to that observed when the contaminated dust sample comprised the surface layer (Tables 11·3 and 11·4). In the former and latter cases, mean values of 21% (n=2) and 23% (n=3) of the applied cadmium (respectively) were detected in the 0–1 cm layer. In both cases no additional cadmium was detected in soil of depth exceeding 1 cm. The similarity of the results suggests that cadmium in both contaminated materials may have been either present in similar forms at the beginning of the experiments, or converted to similar forms during the course of the experiments. It would be expected that at pH 6.85 a large proportion (≈90%) of the cadmium added to the Tai Tapu silt loam from the standard solution would become adsorbed onto the soil's surface (section 10·3·2), and it is possible that this could also be true of cadmium in the contaminated dust sample.

The results of all experiments in which leaching solutions of pH 4.70 were used are listed in Appendices 11·2 and 11·3. That data in Appendices 11·2 and 11·3 which relates to cadmium and zinc mobilities is illustrated in Figure 11·2.

Figure 11·2

Depth-profiles (graphed as a percentage of the amount applied) of additional cadmium and zinc in soil columns treated with 1 155 ml of acetic acid/sodium acetate buffer of pH 4.70.
Note: *Spiked soil # 1 and # 2* refer to cases where cadmium was originally applied to the columns in the form of the cadmium-spiked Tai Tapu silt loam; *contaminated dust # 3 and # 4* refer to the cases where the leaching solution was added in 100 ml increments.





Decreasing the pH of the leaching solutions from 6.85 to 4.70 (but using the same volumes) caused the mobilities of cadmium, copper and zinc in Tai Tapu silt loam to increase, but had no effect on the mobility of lead (Figure 11·2 and Appendix 11·2). Mean losses of cadmium, copper, lead and zinc from the contaminated surface layers at pH 4.70 were 61%, 52%, 19% and 68%, respectively; figures which are higher than values at pH 6.85 by factors of 2.8 for cadmium, 50 for copper (1 for lead) and 4.5 for zinc. Relative mobilities of the four metals at pH 4.70 are in the order cadmium ≈ zinc > copper > lead.

The increased mobilities of cadmium, copper and zinc observed at higher acidities are likely to be caused both by increased competition by hydrogen ions for adsorption sites, and greater stability of these metals' simple ionic species at higher acidities. The pH values below which simple ionic (*i.e.* mobile) species of the four metals studied are thermodynamically stable are: cadmium (pH 8) > zinc (pH 7) > copper (pH 6) > lead (pH 2) (Hermann and Neumann-Mahlkau, 1985); a sequence which compares well with the observed mobilities of the metals in Tai Tapu silt loam at pH 4.70.

Additional cadmium and zinc penetrated to a depth of 3–4 cm, and the depth-profiles of (extra) cadmium and zinc under these conditions were found to be quite similar (Figure 11·2). Although cadmium is one of the two most mobile metals at pH 4.70, in absolute terms its mobility in Tai Tapu silt loam was still seen to be rather limited, a result which probably reflects (once again) the high affinity of Tai Tapu silt loam for cadmium (section 10·3·2).

Despite the fact that approximately 50 times more copper was removed from the surface layer using a leaching solution of pH 4.70 than was the case with a leaching solution of pH 6.85, additional copper in the former experiment was detected to only twice the depth of soil (1–2 cm) than it was in the latter (0–1 cm). Divalent copper (Cu^{2+}), which is stable below pH 6, would be unlikely to form at pH 6.85 but likely to form at pH 4.70, and is probably the species responsible for the sharp increase in the amount of copper lost from the surface layer (Hermann and Neumann-Mahlkau, 1985). Hindrance to the movement of simple ionic copper through the soil may have been supplied by organic matter complexing the metal upon its entry into the soil column, both because copper can be strongly complexed by organic matter in the soil (Brown *et al.* 1983), and because organic matter comprised 12% of the Tai Tapu silt loam.

No significant differences exist in the mobilities of cadmium, copper, lead or zinc between the soil columns through which a volume of pH 4.70 leaching solution equivalent to the average annual rainfall was passed in a continuous manner, and the soil columns through which the same total volume of (pH 4.70) leaching solution was passed in 100 ml increments (allowing time for drainage) (Appendix 11·2). (All four columns were covered with a layer of the contaminated dust sample.) This result suggests that the intermittent nature of rainfall may not be a particularly important factor in determining the mobilities of cadmium, copper, lead, or zinc in soils.

Cadmium deposited on the soil columns in the form of the cadmium-spiked Tai Tapu silt loam appears to be slightly less mobile at pH 4.70 than cadmium applied in the form of

the contaminated dust sample (Figure 11·2 and Appendices 11·2 and 11·3). Additional cadmium in the former two columns was detected in soil from a depth of 2–3 cm, whereas that in three of the four latter cases penetrated to 3–4 cm soil depth. However, a large part of this difference could be due to analytical errors, as the mean recovery of cadmium from the two columns covered with the spiked Tai Tapu silt loam was only 77% (compared with 96% for the columns which were covered with the contaminated dust sample).

Results of experiments in which leaching solutions of pH 3.00 were passed through two 20 cm soil columns, each covered with a layer of the contaminated dust, are listed in Appendix 11·4, from which Figure 11·3 is derived.

Figure 11·3

Depth-profiles (graphed as percentages of amounts applied) of additional cadmium, copper and zinc in the two soil columns covered with a layer of the contaminated dust and leached with acetic acid/sodium acetate buffers of pH 3.00.

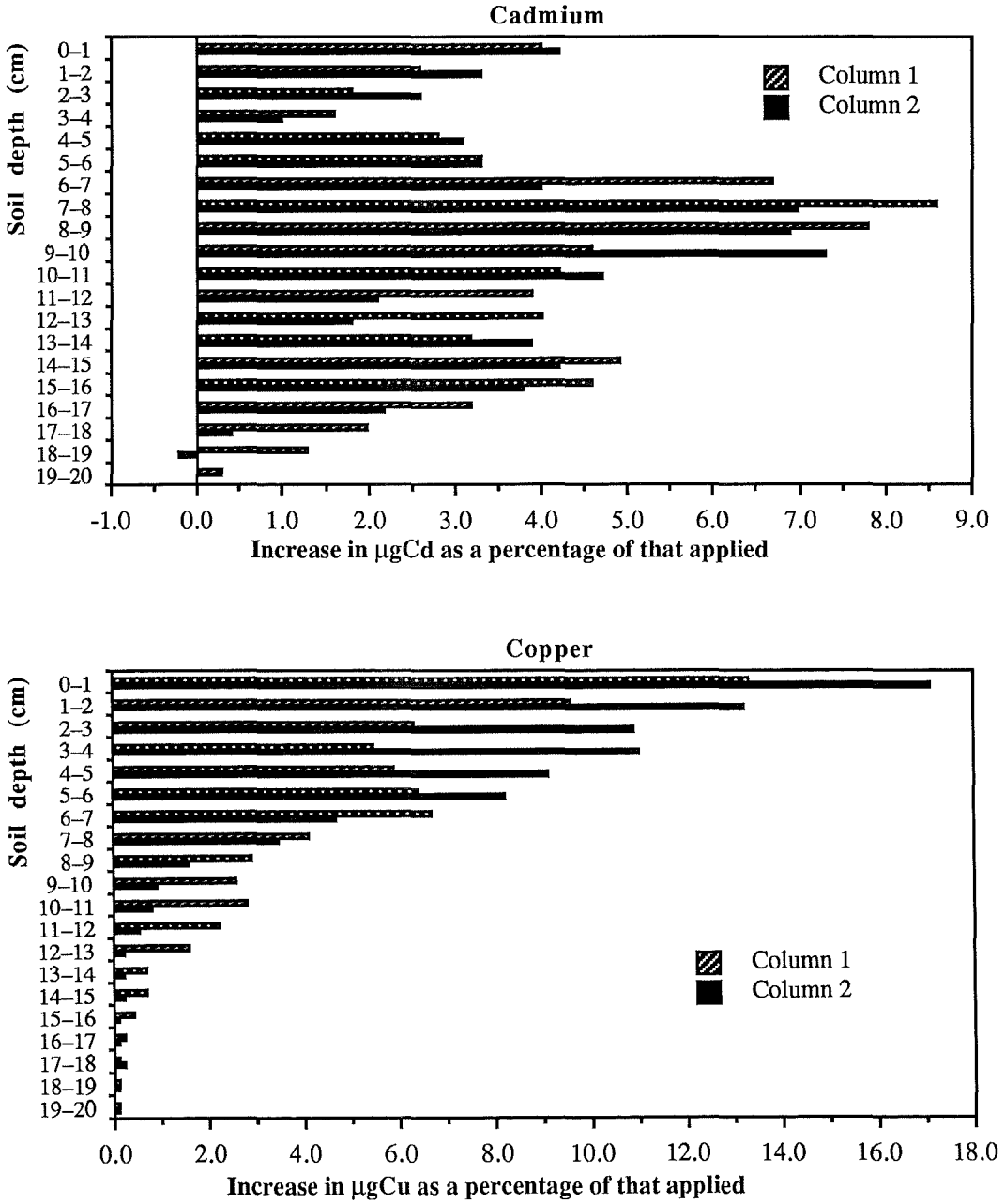
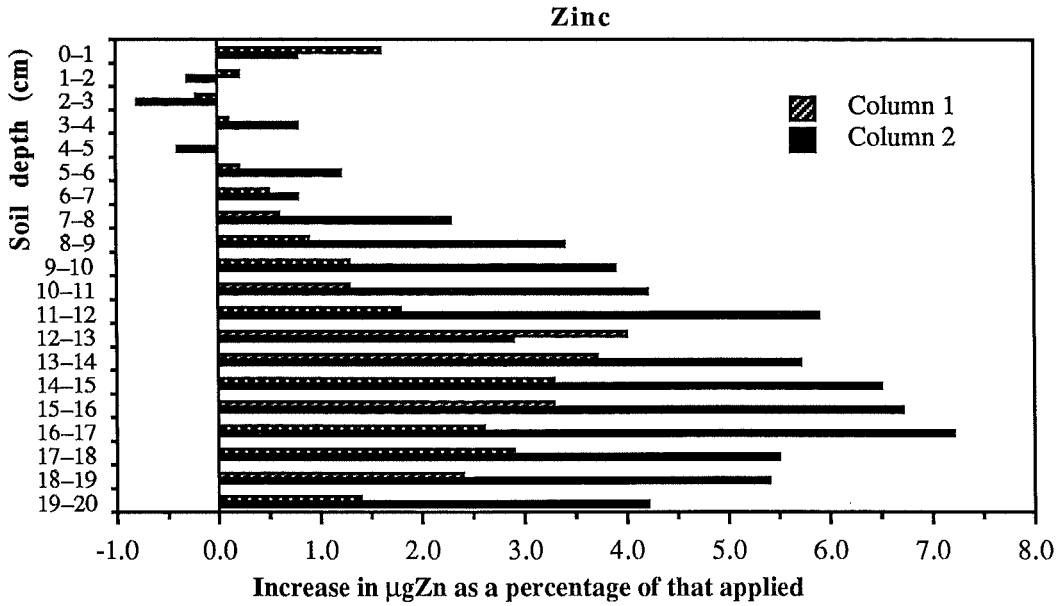


Figure 11·3 continued...



The leaching experiments involving leaching solutions of pH 3.00 were conducted primarily to achieve a better "chromatographic" type separation of the four metals, and this was indeed the effect (Figure 11·3 and Appendix 11·4). Relative mobilities of the four metals at pH 3.00 follow the order zinc > cadmium > copper > lead. Mean losses of cadmium, copper, lead and zinc from the contaminated surface layers increased to 85%, 88%, 47% and 83%, respectively; figures which are higher than values at pH 4.70 by factors of 1.4 for cadmium, 1.7 for copper, 2.6 for lead and 1.2 for zinc. Levels of the metals in the leachates were not measured; however, mean recoveries of cadmium, copper, lead and zinc within the soil columns were 86%, 84%, 93% and 66%, respectively.

Under these conditions, the depth-profile of additional cadmium becomes distinct from that of zinc, and shows peaks at three soil depths: 0–2 cm, 6–10 cm and 13–17 cm (Figure 11·3). These peaks could correspond to different cadmium species in the contaminated surface layer showing varying solubilities in pH 3.00 acetic acid/sodium acetate buffer, a topic which is discussed in further detail in section 11·3·4.

The depth-profile of extra zinc (Figure 11·3) and the low mean recovery for this metal (66%) suggests that a large fraction of the added zinc passed through the 20 cm soil column and into the leachate. The highest amounts (μg) of additional zinc under these conditions were found in soil from depths of between 12 and 18 cm (Figure 11·3 and Appendix 11·4).

The amount of additional copper is highest in the 0–1 cm layer, and declines fairly steadily with depth to at least 15 cm (and possibly to 20 cm) (Figure 11·3). This large increase in copper's mobility at pH 3.00 (compared with its mobility at pH 4.70) could be due to a decreased ability of soil organic matter to complex copper at pH 3.00 (Brown *et al.* 1983).

Once again, lead was the least mobile of the four metals, with additional lead being (reliably) detected to a maximum soil depth of only 2 cm (Appendix 11·4). However, lead

showed the greatest increase of the four metals in the amount lost from the surface layer upon changing the pH of the leaching solutions from 4.70 to 3.00. This behaviour may have been a result of the acidity of the leaching solutions (pH 3.00) moving closer to that required for large-scale stabilization of simple ionic lead (pH 2) (Hermann and Neumann-Mahlkau, 1985).

Summaries of the effect of pH changes on the maximum depths of soil penetration attained by each of the four metals, and on the percentages of cadmium, copper, lead and zinc lost from the contaminated dust sample, are given in Table 11·5.

Table 11·5

Percentages of cadmium, copper, lead and zinc lost from the contaminated dust sample and the maximum depths (cm) of soil penetration attained by the four metals using rainwater and buffers of pH 6.85, 4.70 and 3.00 as leaching solutions.

	Cadmium	Copper	Lead	Zinc
% of metal lost from surface layer (contaminated dust sample)				
pH 6.85	21	1	19	15
Rainwater (pH 5.18)	29	(–3)	8	23
pH 4.70	61	52	18	68
pH 3.00	85	88	47	83
Maximum[a] depth of soil penetration (cm)				
pH 6.85	1	1	1	1
Rainwater (pH 5.18)	1	1	1	1
pH 4.70	4	2	1	4
pH 3.00	20	18	2	>20

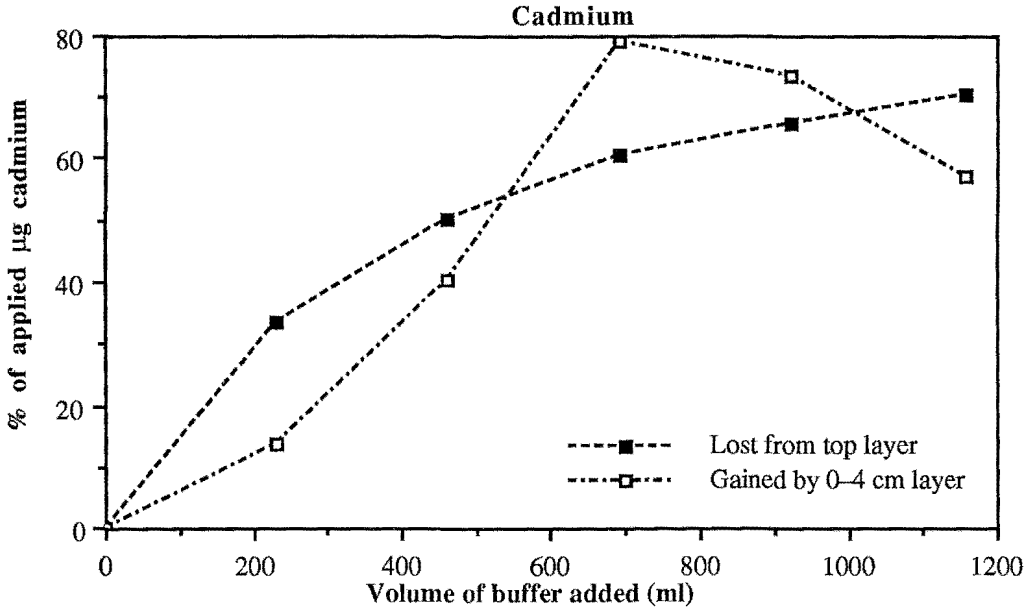
Note: **a.** Maximum likely depth taking depth-profile trends and probable errors into account.

11·3·3 Effect of varying the volume of leaching solution added

Results of the experiments in which pH 4.70 acetic acid/sodium acetate buffers of total volumes corresponding to 20%, 40%, 60% and 80% of the average annual rainfall were passed through four leaching columns (each covered with a layer of the contaminated dust) are given in Appendix 11·2. The percentages of cadmium, copper, lead and zinc lost from the surface layer (contaminated dust) and gained by the 0–4 cm soil layer using total volumes of leaching solution of 231 ml, 462 ml, 693 ml, 924 ml and 1 155 ml (added to separate columns) are graphed together in Figure 11·4. The maximum soil depths to which additional cadmium, copper, lead and zinc were detected under these conditions are listed in Table 11·6.

Figure 11·4

Percentages of cadmium, copper, lead and zinc lost from the surface layer (contaminated dust) and gained by the 0–4 cm soil layer using total volumes of buffer of 231 ml, 462 ml, 693 ml, 924 ml and 1 155 ml.



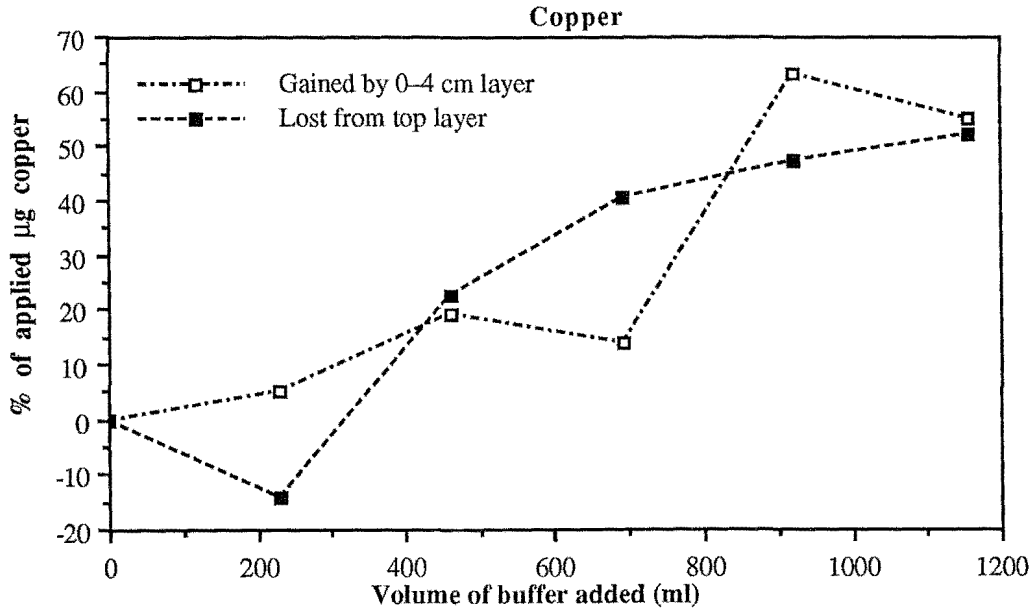
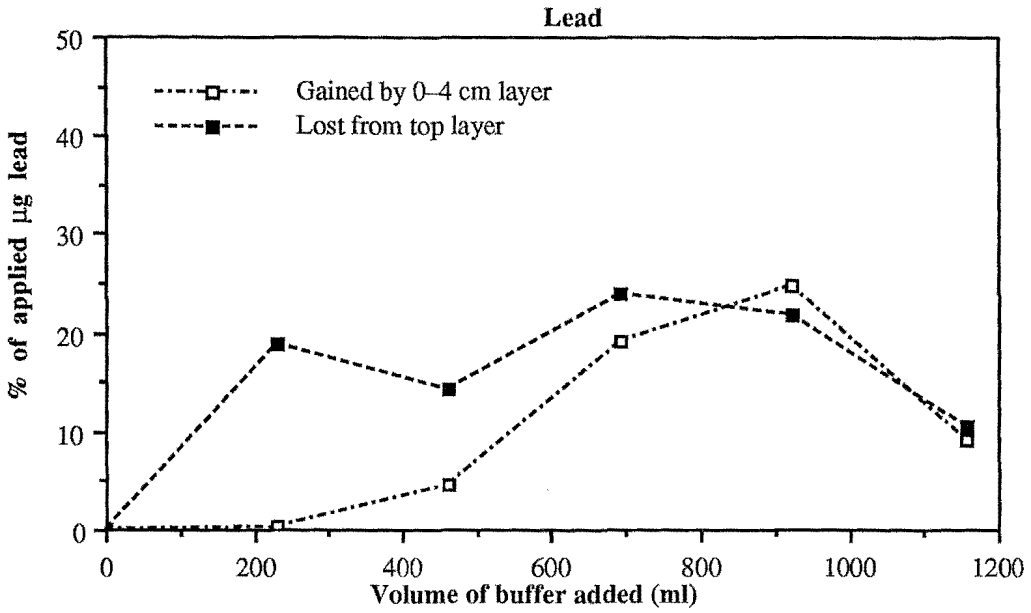


Figure 11·4 continued...



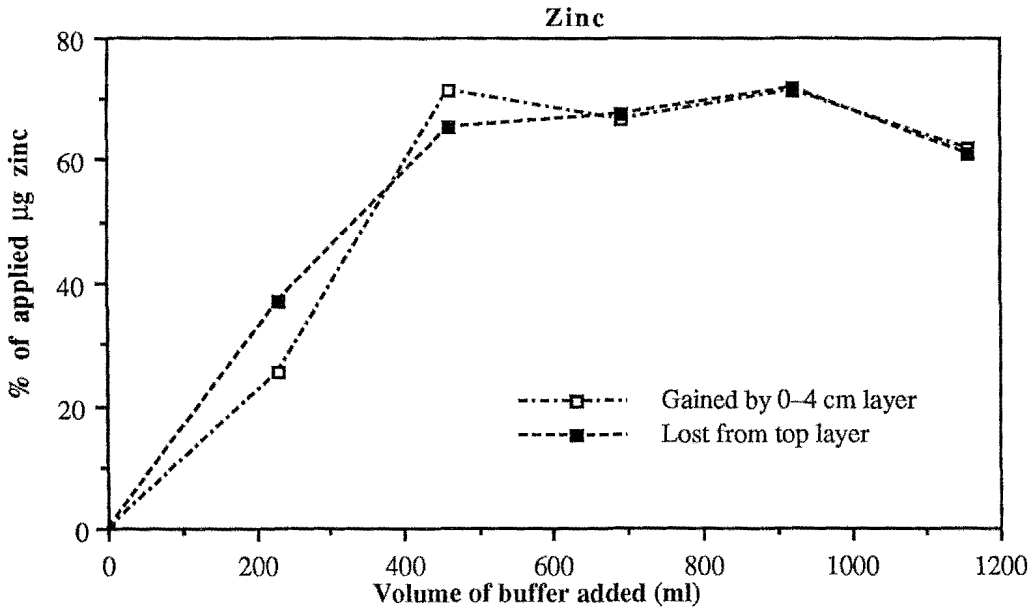


Table 11·6

Maximum soil depths to which additional cadmium, copper, lead and zinc were detected when using volumes of pH 4.70 buffer corresponding to 20%, 40%, 60%, 80% and 100% of the average annual rainfall.

Volume of buffer added (ml)	Soil depth additional metal detected (cm)			
	Cadmium	Copper	Lead	Zinc
231	2	2	1	3
462	3	2	1	4
693	4	2	1	4
924	4	2	1	4
1 155[a]	4	2	1	4

Note: **a.** Results given in section 11·3·2; mean of the four columns.

The following observations can be made from Figure 11·4 and from the data in Table 11·6 and Appendix 11·2 (231 ml, 462 ml, 693 ml, 924 ml and 1 155 ml of leaching solution will be referred to as 20%, 40%, 60%, 80% and 100% of the *equivalent annual rainfall*, respectively):

1. Loss of cadmium from the contaminated surface layer at pH 4.70 was rapid at first, with addition of 20% and 40% of the equivalent annual rainfall causing losses of 33% and 50% (respectively) of the amount of cadmium in the contaminated layer, and movements of the leached cadmium to soil depths of 2 cm and 3 cm (respectively)—trends which suggest that a large proportion of the leachable cadmium is relatively easily mobilized. From there the overall loss of cadmium experienced by the surface layer upon addition of the three further 20% increments of the equivalent annual rainfall increased in a slower but more or less linear manner, and the leached cadmium was detected in soil to only one more centimetre depth (4 cm). The trend shown by the graph relating to cadmium in Figure 11·4 suggests addition of leaching solution in excess of 100% of the equivalent annual rainfall would cause further cadmium to be leached from the surface layer.
2. All (or almost all) of the pH 4.70-leachable zinc in the contaminated surface layer was mobilized upon addition of the first 40% of the equivalent annual rainfall; addition of 60%, 80% and 100% of the equivalent annual rainfall had much the same effect as addition of 40%. Reflecting these results, the leached zinc penetrated the soil to a depth of 3 cm upon addition of 20% of the equivalent annual rainfall, but moved no further than 4 cm upon addition of 40%, 60%, 80% or 100% of the equivalent annual rainfall.
3. In contrast to the trends shown by cadmium and zinc, copper leached from the contaminated surface layer (and into the 0–4 cm layer) in a more or less linear manner ($R = 0.924$, $p = 0.025$) with the volume of (pH 4.70) leaching solution added (and it appears likely that addition of leaching solution in excess of 100% of the equivalent

annual rainfall would cause further losses of copper from the surface layer). However, despite this, the leached copper penetrated the soil to a depth of (only) 2 cm regardless of the amount of leaching solution added; it is possible that soon after entering the soil column, simple ionic copper may have been complexed and immobilized by soil organic matter.

4. The amounts of lead leached from the contaminated surface layer at pH 4.70 were relatively low (Appendix 11·2), but appear to be largely independent of the volume of leaching solution added (Figure 11·4), suggesting that a small fraction of the lead in the contaminated dust sample may be readily mobilized by pH 4.70 leaching solution. In no case was the mobilized lead detected in soil from below 1 cm depth.

11·3·4 Effect of speciation on the mobility of cadmium in soil

Results of the three mobility experiments which involved the leaching of cadmium (with 1 155 ml acetic acid/sodium acetate buffers of pH 3.00) from silica sand-diluted cadmium carbonate, cadmium oxide and cadmium sulphide are given in Table 11·7. Figure 11·5 is derived from the data in Table 11·7.

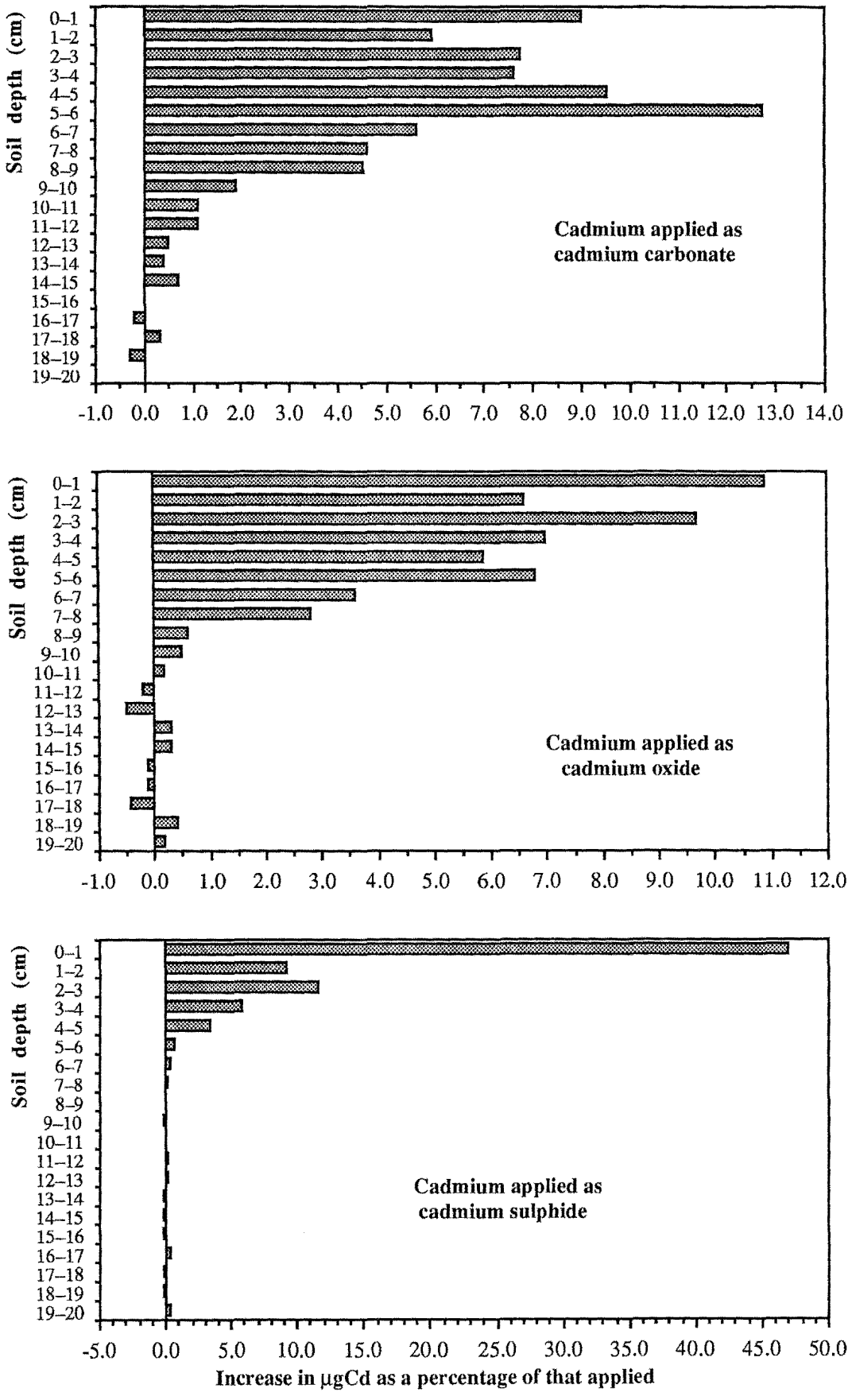
Table 11·7

Results relating to the leaching of cadmium from silica sand-diluted cadmium carbonate, cadmium oxide and cadmium sulphide through 20 cm soil columns, using in each case 1 155 ml of 0.01 M pH 3.00 acetic acid/sodium acetate buffer as the leaching solution.

	Composition of top layer					
	Soil spiked with $CdCO_3$		Soil spiked with CdO		Soil spiked with CdS	
	Total µg	Percent	Total µg	Percent	Total µg	Percent
Top layer: original	29.6	100	29.6	100	29.6	100
after leaching	0.031	–99.9	0.027	–99.9	0.809	–97.3
Gained by soil:						
0–1 cm	2.67	9.0	3.22	10.9	13.9	47.0
1–2 cm	1.76	5.9	1.96	6.6	2.73	9.2
2–3 cm	2.28	7.7	2.87	9.7	3.41	11.5
3–4 cm	2.26	7.6	2.08	7.0	1.73	5.8
4–5 cm	2.81	9.5	1.75	5.9	0.962	3.3
5–6 cm	3.76	12.7	2.01	6.8	0.184	0.6
6–7 cm	1.65	5.6	1.08	3.6	0.104	0.4
7–8 cm	1.35	4.6	0.842	2.8	0.021	0.1
8–9 cm	1.33	4.5	0.181	0.6	0.004	0
9–10 cm	0.556	1.9	0.158	0.5	–0.028	–0.1
10–11 cm	0.324	1.1	0.052	0.2	–0.008	0
11–12 cm	0.316	1.1	–0.067	–0.2	0.066	0.2
12–13 cm	0.154	0.5	–0.151	–0.5	0.042	0.1
13–14 cm	0.125	0.4	0.089	0.3	–0.063	–0.2
14–15 cm	0.202	0.7	0.074	0.3	–0.021	–0.1
15–16 cm	0.013	0	–0.032	–0.1	–0.045	–0.2
16–17 cm	–0.051	–0.2	–0.018	–0.1	0.075	0.3
17–18 cm	0.098	0.3	–0.122	–0.4	–0.046	–0.2
18–19 cm	–0.096	–0.3	0.108	0.4	–0.044	–0.2
19–20 cm	0	0	0.046	0.2	0.090	0.3
Leachate:	5.00	16.9	5.21	17.6	4.28	14.5
Recovery:	26.5	89.5	21.4	72.3	28.2	95.1

Figure 11·5

Depth-profiles of extra cadmium in the three soil columns which were covered with silica sand-diluted cadmium carbonate, cadmium oxide and cadmium sulphide, and leached with buffers of pH 3.00.



It can be seen from Figure 11·5 and the data in Table 11·7 that at pH 3.00 the mobility of cadmium in Tai Tapu silt loam is highly dependent on the form of cadmium deposited on the soil surface. Cadmium applied as cadmium carbonate was the most mobile, and penetrated the soil to a depth of about 15 cm; the depth-profile of additional cadmium in this column shows a peak at 5-6 cm. Cadmium deposited on the soil surface in the form of cadmium oxide, and that applied as cadmium sulphide, attained soil depths of (about) 11 cm and 6 cm (respectively), and thus rank second and third in terms of mobility. The depth-profiles of extra cadmium in these latter two cases both peak in the 0–1 cm soil layer; however, the "band of cadmium enrichment" is broader in the column originally covered with cadmium oxide than it is in the case of the column originally covered with cadmium sulphide (Figure 11·5).

Assuming that the predominant mobile species of cadmium was in all three cases the divalent cadmium ion—which is thought likely—the differences observed must be due to the three cadmium compounds having different solubilities in the acetic acid/sodium acetate buffer of pH 3.00. All three compounds are reported to be insoluble in water (Weast and Astle, 1983). However, carbonates (including cadmium carbonate) are dissolved in pH 5.00 acetic acid/sodium acetate buffers in sequential extraction schemes (Tessier *et al.* 1979); conversely, cadmium sulphide is regarded as one of the least soluble cadmium compounds commonly encountered in the environment (Hermann and Neumann-Mahlkau, 1985). It was also found during the course of this study that 100 ml of acetic acid/sodium acetate buffer of pH 3.00 was sufficient to completely dissolve 1 g samples of solid cadmium carbonate, and partially dissolve 1 g cadmium oxide and cadmium sulphide samples.

Taking these observations into account, it would seem likely that the high mobility of cadmium in the soil column originally covered with (diluted) cadmium carbonate is due to that compound's rapid dissolution in the acetic acid/sodium acetate buffer—most or all of the leachable cadmium in that sample was likely to have been converted to the mobile (simple ionic) form a short time after the experiment began. Conversely, the limited solubility of cadmium sulphide in the acetic acid/sodium acetate buffer of pH 3.00 was probably the cause of cadmium's relative immobility in the cadmium sulphide-covered soil column. Cadmium oxide's solubility in the leaching solution presumably falls somewhere between the solubilities of cadmium carbonate and cadmium sulphide.

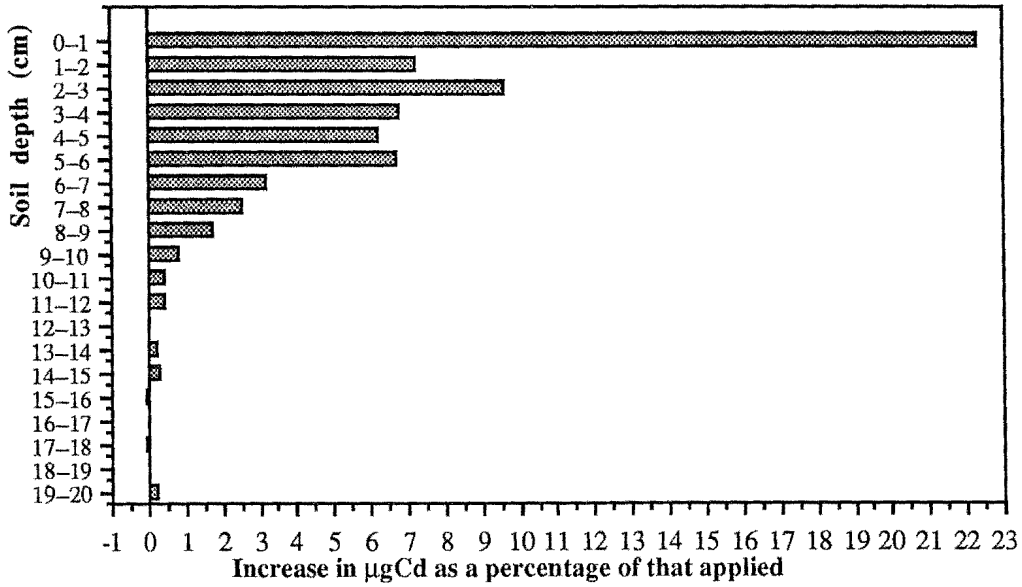
Interestingly, the amount of cadmium in the leachates of the three columns was similar (and quite high), ranging from 14.5% to 17.6% of the amount applied to the soil surfaces. This result does not necessarily represent cadmium leached from the surface layer, as the low pH may have caused movement of the "background" cadmium from the soil within the columns (the Tai Tapu silt loam contained 0.096 $\mu gCd\ g^{-1}$, Appendix 11·1). Each centimetre of soil from the columns weighed about 4.5 g, implying that each 20 cm soil column contained about 8.6 μg of "background" cadmium. After the experiments, leachates from the three columns contained a mean value of 4.8 μg cadmium (standard deviation 0.5 μg cadmium), a figure which could be entirely accounted for by displacement of

cadmium from the lower 11–12 cm of the soil columns (and its replacement by downward leaching of cadmium from the shallower depths).

It was seen in section 11·3·2 that the soil depth-profile of additional cadmium leached from the contaminated dust sample using an acetic acid/sodium acetate leaching solution of pH 3.00 showed three peaks (Figure 11·3). From the preceding discussion it seems likely that these peaks corresponded with cadmium species of differing solubility in the original contaminated layer. It is also possible that cadmium carbonate, cadmium oxide and cadmium sulphide may have been the species concerned. A composite graph, constructed from the mean values of the relative percentages of cadmium at each soil depth over the three columns to which silica-sand diluted cadmium compounds were added, is presented in Figure 11·6.

Figure 11·6

Graph of the mean values of the relative percentages of cadmium at each soil depth over all three columns to which silica sand-diluted cadmium compounds were applied.



The (additional cadmium) depth-profile depicted in Figure 11·6 is what might be expected if a soil column covered with a contaminated surface layer comprising equal amounts of cadmium carbonate, cadmium oxide and cadmium sulphide (to a total cadmium content of 29.6 µg) were leached with 1 155 ml of acetic acid/sodium acetate buffer of pH 3.00.

It can be seen from Figure 11·6 that the composite depth-profile has peaks of cadmium enrichment corresponding to soil column depths of 0–1 cm, 2–3 cm and 5–6 cm. These figures do not compare particularly well with the positions of the three peaks observed in the case of the contaminated dust sample which was leached under the same conditions, which appeared at soil depths of 0–2 cm, 6–10 cm and 13–17 cm (Figure 11·3). However, in the latter case, high amounts of copper and zinc were simultaneously leaching through the soil (Figure 11·3 and Appendix 11·4), and competition of these metals for soil exchange sites

may have effectively enhanced cadmium's mobility (section 10·3·4). (In the original contaminated dust sample, the concentrations of copper and zinc were 543 and 215 times higher than that of cadmium, respectively.) If it could be assumed that the presence of copper and zinc caused cadmium's mobility to increase by a factor of 3, and the positions of peaks in the columns covered with the silica sand-diluted cadmium compounds were adjusted for this factor, the expected peaks in the presence of competing metal ions in these columns would be at depths of 0–3 cm, 6–9 cm and 15–18 cm.

Thus, it remains conceivable that the species cadmium carbonate, cadmium oxide and cadmium sulphide were responsible for the peaks observed in the cadmium depth-profiles of the soil columns which were covered with the contaminated dust sample and leached with buffers of pH 3.00.

Under environmental conditions, differences in the mobility of cadmium applied to the soil as cadmium carbonate, cadmium oxide or cadmium sulphide would be dependent on the solubility of each species in natural water; under such conditions, mobility differences may be small.

Refinement of this techniques outlined in this section could provide another means of experimentally determining trace metal speciations.

11·4 Conclusion

Leaching of two contaminated dust samples, which initially contained 36.8 μgCd g^{-1}, 20 mgCu g^{-1}, 7.42 mgPb g^{-1} and 7.90 mgZn g^{-1}, with volumes of Christchurch rainwater (pH 5.18) equivalent to the average annual rainfall, caused little movement of cadmium, copper, lead or zinc—either from the contaminated surface layers, or through the soil columns. Under these conditions, none of the four metals penetrated to soil depths below 1 cm, and concentrations in the leachates remained below analytical detection limits (<0.2 μgCd l^{-1}, <0.04 μgCu ml^{-1}, <0.11 μgPb ml^{-1} and <0.01 μgZn ml^{-1}). The relative mobilities of the four metals when using rainwater as the leaching solution were in the order cadmium $\approx$ zinc > copper $\approx$ lead.

In terms of cadmium, these findings suggest that under environmental conditions, the mobile fraction of a cadmium-containing substance which is applied to a (Christchurch) soil surface is likely to be available to plant roots in the short-to-medium term (1–5 years), but is unlikely to leach to the ground-water, a conclusion which is in general agreement with those implied by the results of the cadmium adsorption experiments (Chapter 10).

Results obtained by use of leaching solutions buffered at pH 6.85 were more or less identical to those obtained by use of rainwater. Raising the acidity of the buffered leaching solutions to pH 4.70 caused fourfold increases in the mobilities of cadmium and zinc and a twofold increase in the mobility of copper in the soil columns, but had little or no effect on the mobility of lead. Further increasing the acidity to pH 3.00 caused the metals' soil mobilities to increase over those observed at pH 4.70 by a factor of nine for copper, greater than five for zinc, five for cadmium, and two for lead. Relative mobilities of the four metals

in Tai Tapu silt loam at pH 3.00 follow the order zinc > cadmium > copper > lead. The increased mobilities observed at higher acidities are likely to be caused both by increased competition by hydrogen ions for adsorption sites, and an increased stabilization of the simple ionic species of cadmium, copper, lead and zinc at higher acidities.

Zinc loss from the contaminated surface layer at pH 4.70 was found to be a comparatively fast process, with most or all of the pH 4.70-leachable zinc being mobilized by addition of the first 40% of the volume of leaching solution eventually added (which was equivalent in volume to the average annual rainfall). Similarly, overall loss of cadmium from the contaminated surface layer (at pH 4.70) was fairly rapid at first, and thereafter increased in an approximately linear manner. In contrast, loss of copper from the contaminated surface layer was linearly related to the the volume of (pH 4.70) leaching solution added, and the loss of lead appeared to be small and largely independent of the volume of leaching solution added.

Substitution of the phosphate-containing buffer (pH 6.85) with an acetate-containing buffer of the same pH had little effect on cadmium's mobility, implying that cadmium's movement was not significantly inhibited by the presence of phosphate anions. Similarly, use of cadmium-spiked Tai Tapu silt loam instead of the contaminated dust sample as the surface layer had no effect on cadmium mobility at pH 6.85, and the results relating to a similar experiment at pH 4.70 were seen to be ambiguous, due to the low overall cadmium recoveries from columns covered with the cadmium-spiked Tai Tapu silt loam. Intermittent addition of the pH 4.70 leaching solutions (allowing time for drainage) was also found to have little or no effect on the mobilities of the four metals in Tai Tapu silt loam, suggesting that the non-continuous nature of rainfall may not be a particularly important factor governing the rates of leaching of the four metals in soils.

The mobility of cadmium in Tai Tapu silt loam at pH 3.00 is highly dependent on the form or forms of cadmium deposited on the soil surface. Cadmium applied to the soil surface in the form of cadmium carbonate was more mobile than cadmium applied as cadmium oxide, which was in turn more mobile than cadmium deposited in the form of cadmium sulphide. It is thought likely that these variations in cadmium's mobility were a direct result of the different solubilities of the three cadmium compounds in the buffer of pH 3.00. It is also thought probable that the different solubilities of cadmium species originally present in contaminated dust sample caused the three peaks observed in the (additional) cadmium depth-profiles of the soil columns which were covered with contaminated dust and leached with buffers of pH 3.00.

11·5 References

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11·6 Appendices

Appendix 11·1 (section 11·2)

Means, standard deviations and 95% confidence intervals for the concentrations of cadmium, copper, lead and zinc in Tai Tapu silt loam.

	Cadmium	Copper	Lead	Zinc
Number of analyses	23	16	18	16
Mean concentration ($\mu g\ g^{-1}$)	0.096	19.1	92.8	70.1
Standard deviation ($\mu g\ g^{-1}$)	0.020	2.0	8.9	6.4
95% error on mean[a]	±0.007	±0.9	±3.8	±3.0

Note: a. Student's t-test.

Appendix 11·2 (sections 11·3·2 and 11·3·3)

All results relating to the leaching of cadmium, copper, lead and zinc from the contaminated dust sample using buffers of pH 4.70.

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
231 ml pH 4.70 acetate buffer								
Top layer:								
Original amount	29.3	16 100	5 900	6 290	100	100	100	100
After leaching	19.5	18 400	4 790	3 970	–33.4	+14.3	–18.8	–36.8
Gained by soil:								
0–1 cm	3.33	746	14.8	996	11.4	4.6	0.3	15.8
1–2 cm	0.727	126	0	382	2.5	0.8	0	6.1
2–3 cm	0	0	0	229	0	0	0	3.6
3–4 cm	0	0	0	0	0	0	0	0
Recovery within column	23.6	19 300	4 800	5 580	80.4	120	81.4	88.7
462 ml pH 4.70 acetate buffer								
Top layer:								
Original amount	29.1	16 000	5 950	6 260	100	100	100	100
After leaching	14.5	12 400	5 100	2 180	–50.2	–22.5	–14.3	–65.2
Gained by soil:								
0–1 cm	9.32	2 300	273	1 670	32.0	14.4	4.6	42.8
1–2 cm	2.24	766	0	762	7.7	4.8	0	15.0
2–3 cm	0.195	0	0	367	0.7	0	0	8.2
3–4 cm	0	0	0	188	0	0	0	5.3
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	26.3	15 500	5 420	5 170	90.2	96.7	91.1	82.5
693 ml pH 4.70 acetate buffer								
Top layer:								
Original amount	29.4	16 100	5 990	6 310	100	100	100	100
After leaching	11.6	9 600	4 550	2 040	–60.5	–40.4	–24.0	–67.7
Gained by soil:								
0–1 cm	19.8	1 600	1 140	2 290	67.3	9.9	19.0	36.3
1–2 cm	1.90	674	0	1 290	6.4	4.2	0	20.4
2–3 cm	1.25	0	0	438	4.3	0	0	6.9
3–4 cm	0.290	0	0	184	1.0	0	0	2.9
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	34.8	11 900	5 690	6 240	119	73.8	95.0	98.9

Appendix 11·2 continued...

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
924 ml pH 4.70 acetate buffer								
Top layer:								
Original amount	28.9	15 900	5 900	6 210	100	100	100	100
After leaching	9.83	8 360	4 720	1 740	–66.0	–47.4	–21.9	–72.0
Gained by soil:								
0–1 cm	19.2	9 300	1 460	2 660	66.4	58.5	24.8	42.8
1–2 cm	1.59	608	0	933	5.5	3.8	0	15.0
2–3 cm	0.269	0	0	511	0.9	0	0	8.2
3–4 cm	0.239	0	0	332	0.8	0	0	5.3
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	29.6	18 300	6 180	6 180	108	115	105	99.5
1 155 ml pH 4.70 acetate buffer								
Column # 1								
Top layer:								
Original amount	29.3	16 100	6 095	6 290	100	100	100	100
After leaching	10.4	9 320	6 370	3 040	–64.5	–42.1	+4.5	–51.7
Gained by soil:								
0–1 cm	12.6	5 940	622	2 780	43.0	36.9	10.2	44.2
1–2 cm	3.37	386	0	948	11.5	2.4	0	15.1
2–3 cm	0.527	0	0	206	1.8	0	0	3.2
3–4 cm	0	0	0	0	0	0	0	0
Recovery within column	26.9	15 650	6 990	6 970	91.7	91.1	115	111
Column # 2								
Top layer:								
Original amount	29.2	16 100	6 090	6 280	100	100	100	100
After leaching	6.89	6 140	4 540	1 850	–76.5	–61.9	–25.5	–70.5
Gained by soil:								
0–1 cm	11.4	10 980	486	1 900	38.9	68.2	8.0	30.3
1–2 cm	4.90	403	0	1 290	16.7	2.5	0	20.5
2–3 cm	0.527	0	0	465	1.8	0	0	7.4
3–4 cm	0.166	0	0	210	0.6	0	0	3.3
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	23.9	17 500	5 030	5 720	81.5	109	82.5	91.0

Appendix 11·2 continued...

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
1 155 ml pH 4.70 acetate buffer added in 100 ml increments								
Column # 1								
Top layer:								
Original amount	29.5	16 200	6 020	6 340	100	100	100	100
After leaching	10.9	7 540	4 570	2 240	–63.1	–53.5	–24.1	–64.7
Gained by soil:								
0–1 cm	12.7	6 030	253	1 340	43.1	37.2	4.2	21.1
1–2 cm	3.86	414	0	1 420	13.1	2.6	0	22.3
2–3 cm	0.274	0	0	327	0.9	0	0	5.2
3–4 cm	0.147	0	0	146	0.5	0	0	2.3
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	27.9	14 000	4 820	5 470	94.5	86.3	80.1	86.3
Column # 2								
Top layer:								
Original amount	29.8	16 300	6 070	6 390	100	100	100	100
After leaching	16.9	7 940	4 480	2 390	–43.3	–51.3	–26.1	–62.5
Gained by soil:								
0–1 cm	16.2	3 390	238	2 160	54.3	20.8	3.9	33.8
1–2 cm	1.33	320	33.0	489	4.5	2.0	0.5	7.7
2–3 cm	0.380	0	0	110	1.2	0	0	1.7
3–4 cm	0.143	0	0	0	0.5	0	0	0
4–5 cm	0	0	0	0	0	0	0	0
Recovery within column	35.0	11 650	4 750	5 150	117	71.5	78.2	80.6

Appendix 11·3 (section 11·3·2)

Results relating to the leaching of cadmium from two samples of Tai Tapu silt loam spiked with cadmium (from a standard solution of cadmium sulphate) using acetate buffers of pH 4.70.

Leaching solution	Total µg cadmium		Percent of µgCd deposited	
	Column # 1	Column # 2	Column # 1	Column # 2
1 155 ml pH 4.70 acetate buffer				
Top layer:				
Original amount	29.7	29.8	100	100
Amount after leaching	12.3	11.1	–58.6	–62.8

Appendix 11·3 continued...

Leaching solution	Total µg cadmium		Percent of µgCd deposited	
	Column # 1	Column # 2	Column # 1	Column # 2
Gained by soil:				
0–1 cm	11.4	8.86	38.3	29.7
1–2 cm	1.48	0.273	5.0	0.9
2–3 cm	0.060	0.045	0.2	0.2
3–4 cm	0	0	0	0
Recovery within column	25.2	29.0	85.0	68.0

Appendix 11·4 (section 11·3·2)

Results relating to the leaching of cadmium, copper, lead and zinc from the contaminated dust sample with buffers of pH 3.00.

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Acetate buffer pH 3.00 (1 155 ml)								
Column # 1								
Top layer:								
Original amount	29.7	16 310	6 060	6 380	100	100	100	100
After leaching	6.51	1 740	3 540	838	–78.1	–89.3	–41.5	–86.9
Gained by soil:								
0–1 cm	1.20	2 170	1 910	102	4.0	13.3	31.5	1.6
1–2 cm	0.774	1 570	669	14.2	2.6	9.6	11.0	0.2
2–3 cm	0.533	1 030	–10.5	–14.4	1.8	6.3	–0.2	–0.2
3–4 cm	0.470	892	93.4	8.60	1.6	5.5	1.5	0.1
4–5 cm	0.817	960	34.9	–1.05	2.8	5.9	0.6	0
5–6 cm	0.968	1 040	–14.8	14.5	3.3	6.4	–0.2	0.2
6–7 cm	1.99	1 100	11.1	34.8	6.7	6.7	0.2	0.5
7–8 cm	2.54	675	–20.6	40.7	8.6	4.1	–0.3	0.6
8–9 cm	2.31	440	–10.8	60.3	7.8	2.9	–0.2	0.9
9–10 cm	1.38	418	–9.70	82.1	4.6	2.6	–0.2	1.3
10–11 cm	1.26	449	1.58	115	4.2	2.8	0	1.3
11–12 cm	1.17	354	–34.4	150	3.9	2.2	–0.6	1.8
12–13 cm	1.20	257	–18.9	258	4.0	1.6	–0.3	4.0
13–14 cm	0.956	123	14.4	234	3.2	0.7	0.2	3.7
14–15 cm	1.46	116	29.4	211	4.9	0.7	0.5	3.3
15–16 cm	1.36	65.0	18.6	212	4.6	0.4	0.3	3.3
16–17 cm	0.964	23.0	15.0	167	3.2	0.2	0.3	2.6
17–18 cm	0.592	13.5	11.0	183	2.0	0.1	0.2	2.9
18–19 cm	0.386	14.3	–2.6	150	1.3	0.1	–0.2	2.4
19–20 cm	0.082	15.8	28.2	88.8	0.3	0.1	0.5	1.4
Recovery within column	28.9	13 470	6 120	2 950	97.3	82.6	101	46.3

Appendix 11·4 continued...

Leaching solution	Total µg				Percent of original µg deposited			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Column # 2								
Top layer:								
Original amount	18.6	10 250	3 790	4 020	100	100	100	100
After leaching	1.54	1 340	1 780	836	–91.7	–86.9	–53.0	–79.2
Gained by soil:								
0–1 cm	0.784	1 760	1 310	30.9	4.2	17.1	34.6	0.8
1–2 cm	0.611	1 320	144	–14.6	3.3	13.2	3.8	–0.3
2–3 cm	0.478	1 150	12.7	–30.5	2.6	10.9	0.3	–0.8
3–4 cm	0.192	1 080	14.1	30.6	1.0	11.0	0.4	0.8
4–5 cm	0.571	935	–21.1	–16.7	3.1	9.1	–0.5	–0.4
5–6 cm	0.625	845	44.9	48.4	3.3	8.2	1.2	1.2
6–7 cm	0.757	483	–14.3	34.0	4.0	4.7	–0.4	0.8
7–8 cm	1.31	358	–0.8	93.3	7.0	3.5	0	2.3
8–9 cm	1.29	167	38.6	136	6.9	1.6	1.0	3.4
9–10 cm	1.36	98.3	12.1	157	7.3	0.9	0.3	3.9
10–11 cm	0.886	78.8	–18.5	170	4.7	0.8	–0.5	4.2
11–12 cm	0.395	49.2	–39.5	236	2.1	0.5	–1.0	5.9
12–13 cm	0.338	23.6	–35.3	116	1.8	0.2	–0.9	2.9
13–14 cm	0.725	23.7	–31.4	229	3.9	0.2	–0.8	5.7
14–15 cm	0.798	23.3	–38.8	260	4.2	0.2	–1.0	6.5
15–16 cm	0.712	18.0	–20.5	268	3.8	0.1	–0.5	6.7
16–17 cm	0.420	13.3	–20.6	288	2.2	0.1	–0.5	7.2
17–18 cm	0.068	15.2	–38.4	220	0.4	0.2	–1.0	5.5
18–19 cm	–0.046	17.2	–33.1	218	–0.2	0.1	–0.8	5.4
19–20 cm	–0.004	15.0	–63.6	170	0	0.1	–1.7	4.2
Recovery within column	13.8	9 810	3 230	3 480	74.2	95.7	85.3	86.5

CHAPTER 12
STUDIES IN THE APPLICABILITY OF A SEQUENTIAL EXTRACTION TECHNIQUE FOR DETERMINING CADMIUM'S SPECIATIONS IN SOIL

12·1 Introduction

Trace metals in soils can be associated with several distinct geochemical phases, the most significant of which are considered to be clay minerals, organic matter, iron and manganese oxides, carbonates, and sulphides (Kheboian and Bauer, 1987).

"Phase-selective" chemical fractionation techniques have been extensively used to determine the speciations of trace metals in soils and sediments, information which is useful in estimating the metals' likely mobilities and bioavailabilities (Miller *et al.* 1986; section 1·3·2). In particular, the five-step sequential extraction scheme developed by Tessier *et al.* (1979), has been widely used (Kheboian and Bauer, 1987). Under this scheme, "phase-selective" reagents are used in sequence, and metals are ultimately classified according to the extent to which they are found to be "exchangeable", "bound to carbonates", "bound to organic matter", "bound to iron and manganese oxides" and "associated with residual matter". (The sequential extraction scheme of Tessier *et al.* (1979) is described in more detail in section 12·2.)

In recent years, the accuracy of selective extraction methods has been questioned, for two reasons:

1. Extractants are often non-selective (Jouanneau *et al.* 1983; Kheboian and Bauer, 1987; Miller *et al.* 1986). A reagent designed to selectively dissolve one particular phase (causing the liberation of metals associated with it) may also attack other phases. For example, the method of Tessier *et al.* (1979) employs 30% hydrogen peroxide in acidic solution at 85 °C for the oxidation of organic matter—it is likely partial destruction of clay minerals and manganese oxides in the sample would also occur under these conditions (Van Langeveld *et al.* 1983; Shuman, 1983).
2. Redistribution of metals between phases can occur during the experiment; that is, metals liberated from one phase may become sequestered by one (or more) of the remaining phases within the time-scale of the extraction step. Kheboian and Bauer (1987) observed significant redistribution of copper, lead and zinc between phases when using the sequential extraction scheme of Tessier *et al.* (1979). Other researchers, using other selective extractants, have reported redistributions of arsenic, cadmium, calcium, copper, lead and selenium among various phases of soils and sediments (Gruebel *et al.* 1988; Rendell *et al.* 1980; Tipping *et al.* 1985). Redistribution is dependent upon both the affinity of the remaining undissolved phases for the metal ion involved, and the ability of the extractant used to inhibit the adsorption of the metal by those phases (Kheboian and Bauer, 1987).

The primary aim of this study was to determine whether or not the commonly used sequential extraction scheme of Tessier *et al.* (1979) was likely to provide a reasonably accurate representation of the solid phase-distribution of cadmium in soils (as far as the author is aware, no research has previously been conducted in this area). For this purpose, a range of cadmium-spiked materials and "synthetic soils" with known cadmium phase-distributions were constructed, and then sequentially extracted. Information obtained from these experiments could then be used as an aid in the interpretation of results relating to cadmium from sequential extractions of environmental samples.

12·2 Method

12·2·1 Phase synthesis and characterization, and composition of "synthetic soils"

Calcite (hexagonal calcium carbonate) was prepared by the method of Wray and Daniels (1957). Calcium nitrate solution (AR, 300 ml, 1 M) was added dropwise to a stirred 3 l solution of AR 0.1 M sodium carbonate, and the resulting precipitate was aged for 20 hr in a water bath at 37 °C.

Crystalline goethite (orthorhombic iron oxide hydroxide: α FeO(OH)) was prepared by addition of 200 ml of 2.5 M AR potassium hydroxide solution to 50 g of AR ferric nitrate ($Fe(NO_3)_3.9H_2O$) in 825 ml of double-distilled water, followed by aging of the precipitate for 24 hr at 60 °C (Atkinson *et al.* 1967).

Hausmannite (tetragonal trimanganese tetroxide: Mn_3O_4) crystals were prepared by addition of a solution comprising 550 g of AR sodium hydroxide in 2.5 l double-distilled water to a solution of 300 g of recrystallized CP manganese nitrate hexahydrate ($Mn(NO_3)_2.6H_2O$) in 2 l of double-distilled water. Finely dispersed oxygen gas was passed through the resulting (stirred) mixture for 1 hr. (This method was modified from the recipe given by Wadsley (1950) for the preparation of birnessite ($Mn_{14}O_{27}.8H_2O$).)

Precipitates of clean calcite, goethite, and hausmannite were washed thoroughly with double-distilled water by decantation, oven dried (<30 °C), lightly crushed, and stored in clean air-tight bottles.

Samples of calcite, goethite and hausmannite containing coprecipitated cadmium were prepared by spiking one of the precipitating reagents (calcium nitrate, ferric nitrate and manganese nitrate hexahydrate, respectively) with a measured volume of AR 10 mgCd l^{-1} cadmium sulphate solution. Subsequent analysis by FAAS revealed that 34%, 13% and 12% of the added cadmium was incorporated into the calcite, goethite and hausmannite (respectively). (For these analyses, the calcite was directly dissolved in 2 M nitric acid, the hausmannite was boiled in 4 M nitric acid for 30 minutes, and the goethite was digested in a mixture containing 8 ml of hydrogen fluoride and 3 ml of concentrated nitric acid.) Materials with which cadmium was coprecipitated will be referred to as the *cadmium-coprecipitated* phases throughout this chapter.

X-ray powder diffraction patterns of the clean and cadmium-coprecipitated calcite, goethite and hausmannite were obtained using the methods described in section 5·2. D-spacings (Å) and relative intensities for these species compared well with those listed for the crystalline forms of calcite, goethite and hausmannite in the literature, and are given in Appendix 12·1.

Calcite is frequently found in soils (although its concentration in Tai Tapu silt loam is low), and goethite is the most common form of iron oxide found in soils (Greenland and Hayes, 1978). Hausmannite is not particularly common in soils, but is a stable manganese oxide (with a long shelf-life), and was used for this reason (Moore *et al.* 1950).

Humic acid (Aldrich) was purified to remove residual mineral matter by the method of Weber and Wilson (1975). This involved dissolving the humic acid in 0.01 M AR sodium hydroxide, centrifuging the solution (for 5 minutes at 5 000 r.p.m.) and reprecipitating the humic acid in the decanted supernatant solution by adjusting the pH to 1 (with hydrochloric acid). Humic acid, which is a general name for a broad group of organic acids commonly found in soils which are insoluble in water at pH 1 (Weber and Wilson, 1975), was used as the organic phase of the synthetic soils constructed in this study.

Clay (here taken to represent soil material finer than 3.9 μm) was isolated from the sample of processed Tai Tapu silt loam (section 10·2·1) by the sedimentation technique described in section 10·2·1. Iron and manganese oxides, and organic matter and carbonates were removed from this clay by the methods of Jackson (1958) and Mehra and Jackson (1960) (respectively), which are also outlined in section 10·2·1. The XRPD pattern of the cleaned clay was found to be almost identical to that of the (uncleaned) clay used in the cadmium adsorption experiments, which is given in Appendix 10·1.

Samples of the clean calcite, goethite, hausmannite, humic acid and clay (each weighing 5 g) were placed in 50 ml solutions containing 200 μgCd ml^{-1} (at pH 7.0 and 25 °C) and left for 72 hours, in order to allow cadmium to adsorb onto their surfaces (these materials will be referred to as the *cadmium-sorbed* phases). After equilibration, the cadmium-sorbed phases were washed thoroughly with double-distilled water (by centrifugation) and dried. Portions of these materials were analysed for cadmium by FAAS. (Digestions were as above for calcite, goethite and hausmannite; clay was digested in a mixture containing 8 ml of hydrogen fluoride and 3 ml of concentrated nitric acid, and humic acid was oxidised using 30% hydrogen peroxide at pH 5.8.)

The cadmium concentrations of all the cadmium-spiked materials used in this study are listed in Table 12·1.

Significant abilities to adsorb cadmium were shown by all of the phases listed in Table 12·1; this was seen as an early indication that there was considerable potential for redistribution of cadmium during the course of a sequential extraction. Conditional equilibrium constants for cadmium adsorption under these conditions are in the order hausmannite (6.67 ml g^{-1}) > goethite (6.58 ml g^{-1}) > clay (6.2 ml g^{-1}) > calcite (4.39 ml g^{-1}) > humic acid (1.22 ml g^{-1}).

Table 12·1

Concentrations of cadmium ($\mu g\ g^{-1}$) in the cadmium-coprecipitated and/or cadmium-sorbed calcite, goethite, hausmannite, humic acid and clay used in this study.

Phase	Cadmium-coprecipitated materials	Cadmium-sorbed materials
Calcite	993	610
Goethite	290	794
Hausmannite	253	800
Humic acid		217
Clay		764

It was thought likely that most of the cadmium in the cadmium-coprecipitated phases was incorporated within the crystal lattices of the materials concerned, whereas most of that associated with the cadmium-sorbed phases was on their surfaces. Kheboian and Bauer (1987) used the same techniques as outlined above to spike calcite with lead, mackinawite (FeS) with zinc, goethite and greigite (Fe_3S_4) with copper and nickel, and humic acid with copper, and found (using physical surface analysis techniques) that surface coatings of the metals involved were present on "adsorbed" phases, but not on coprecipitated phases.

Eight "synthetic soils", each spiked with cadmium in a different form, were constructed by mixing (in each case) six of the clean phases with one of the cadmium-spiked phases, and then diluting the mixture with clean silica sand (mentioned in section 10·2·1). Samples were weighed using a four-decimal place balance (to a total weight of 2.000 g $\pm$ 0.002 g) directly into clean glass vials, mixed thoroughly with a clean glass rod, and agitated (at various angles) for 10 minutes. All synthetic soils contained 5% calcite, 10% goethite, 10% hausmannite, 20% humic acid, 15% clay and 40% clean silica sand, ratios which were thought to be reasonably similar to those of the carbonate, iron oxide, manganese oxide, organic matter, clay mineral and sand fractions (respectively) often found in actual soils (Anon. 1968).

The main limitation of the synthetic soils used in this study was their simplicity (in terms of the number and variety of potential cadmium-adsorbing components) when compared with real soils (Kheboian and Bauer, 1987). For this reason, six of the cadmium-spiked materials listed in Table 12·1 were also mixed with measured proportions of the processed Tai Tapu silt loam (in the same ratios as were used for the completely synthetic soils). In no case did the amount of cadmium in the original Tai Tapu silt loam exceed 0.34% of that in the soil when spiked, effectively meaning that the solid state phase-distributions of cadmium in the spiked soils were known. Comparison of experimentally determined with known cadmium phase-distributions in these samples would provide the best estimate of redistributions likely to occur during the sequential extraction of cadmium in real soil systems.

The overall concentrations of cadmium in the synthetic soil mixtures and in the spiked Tai Tapu silt loam samples are listed in Table 12·2.

Table 12·2

Total cadmium concentrations ($\mu g\ g^{-1}$) in the synthetic soils and spiked Tai Tapu silt loam samples.

Soil number	Cd-spiked phase	Form of Cd	Total cadmium concn ($\mu g\ g^{-1}$)	95% error[a] on total Cd concn ($\mu g\ g^{-1}$)
Synthetic soils				
1	Calcite	Coprecipitated	49.7	±2.4
2	Goethite	Coprecipitated	29.0	±1.3
3	Hausmannite	Coprecipitated	25.3	±1.3
4	Humic acid	Adsorbed	43.4	±1.7
5	Clay	Adsorbed	115	±4
6	Calcite	Adsorbed	30.5	±1.5
7	Goethite	Adsorbed	79.4	±3.2
8	Hausmannite	Adsorbed	80.0	±4.0
Spiked Tai Tapu silt loam				
1	Calcite	Coprecipitated	49.7	±2.2
2	Goethite	Coprecipitated	29.1	±1.5
3	Hausmannite	Coprecipitated	25.4	±1.4
4	Humic acid	Adsorbed	43.5	±1.7
5	Clay	Adsorbed	115	±4
6	Calcite	Adsorbed	30.6	±1.5

Note: **a.** Student's t-test.

Total concentrations of cadmium in the synthetic soil mixtures and in the spiked Tai Tapu silt loam samples were relatively high (ranging from 25 to 115 $\mu gCd\ g^{-1}$); these materials could be seen to be representative of soils heavily contaminated with cadmium.

12·2·2 Collection and handling of environmental samples

Samples of road-dust and soil were collected on 17 January 1989. Road-dust samples were collected with a plastic brush and pan from footpaths and roadsides in six industrial areas, and stored in clean plastic bags. Soil cores (of 2.5 cm diameter and 8 cm depth) were obtained from four residential areas with the use of a stainless-steel core extractor, and also stored in clean plastic bags. After collection the soil cores were allowed to air-dry for a period of 48 hr. Samples of house dust were collected using a standard vacuum cleaner from three different Christchurch houses in March 1989. A composite sample of house-dust, representing 120 Christchurch houses, was also gathered during the house-dust survey (Chapter 4), using the vacuuming technique outlined in section 4·2·1. One extra sample was collected for this purpose from each house. Samples from the 120 houses were scraped into a single plastic bag and homogenized.

Road-dust, house dust and soil samples were oven-dried (to constant weight) at 60 °C. This fairly low temperature was chosen in order to minimize possible changes in

cadmium's solid state speciations which may have occurred during the drying process. Samples were then sieved, with particles finer than 563 μm being retained and placed in fresh plastic bags, and homogenized. Samples of road-dust, house-dust and soil (weighing about 0.5 g) were digested in a mixture containing 8 ml of AR hydrogen fluoride and 3 ml of AR nitric acid, filtered, and analysed for total cadmium by GFAAS (using the parameters given in section 3·2·2 and Chapter 14).

12·2·3 Sequential extraction methodology and analysis of samples

Portions of the synthetic soil mixtures, the spiked Tai Tapu silt loam samples and the environmental samples weighing (0.5000 ± 0.0010) g were measured into clean plastic 50 ml centrifuge tubes. Samples of the individual cadmium-spiked phases with weights corresponding to their weights in 0.5 g samples of the synthetic soil mixtures (*viz.* 0.025 g calcite, 0.05 g goethite, 0.05 g hausmannite, 0.1 g humic acid and 0.075 g clay) were also weighed into centrifuge tubes.

The sequential extraction method of Tessier *et al.* (1979) was used throughout this study. The reagents and conditions used in this method (and the fractions which they were intended to solubilize) were as follows:

1. *Exchangeable cadmium:* 8 ml of 1M AR magnesium chloride solution was added to each sample. The mixture was continuously agitated (using a mechanical shaker) for 1 hour and then centrifuged (5 000 r.p.m. for 20 minutes). The supernatant solution was retained for analysis and the residue was washed with 8 ml of double-distilled water (using the centrifuge). It would be expected that a large part (but not necessarily all) of the cadmium in the cadmium-sorbed phases would be liberated during this first extraction step (Tessier *et al.* 1979; Kheboian and Bauer, 1987).
2. *Cadmium bound to carbonates:* 8 ml of 1M ar acetic acid/ sodium acetate buffer of pH 5.0 was added to the residue of step 1, and the resulting mixture was continuously agitated for 5 hours. After this time the solution was centrifuged, the supernatant retained and the residue washed (as in step 1). In addition to the dissolution of carbonates, it might also be expected that this step would liberate specifically adsorbed cadmium which had not been removed in step 1, due to the increased acidity (Tessier *et al.* 1979).
3. *Cadmium associated with easily reducible manganese oxides and amorphous iron oxides:* to the residue of step 2 was added 20 ml of 0.04 M AR hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% AR acetic acid. This solution was left in a water bath at 95 °C for 6 hours (and occasionally agitated). The solution was then centrifuged, the supernatant retained and the residue washed (as in the preceding steps). It was expected that the reagents used in this step would (partially or completely) dissolve the synthetic hausmannite, but have little effect on the crystalline goethite (Gruebel *et al.* 1988; Kheboian and Bauer, 1987).
4. *Cadmium bound to organic matter (and other oxidisable material):* to the residue of step 3 was added 3 ml of 0.02 M AR nitric acid and 5 ml of 30% hydrogen peroxide at

pH 2; this mixture was left (in a water bath) at 85 °C for 5 hours and occasionally agitated. After 2 hours, a second 3 ml aliquot of the acidified 30% hydrogen peroxide was added. Following this treatment, 5 ml of 3.2 M AR ammonium acetate in 20% nitric acid was added to the solution, which was then diluted to 20 ml, mechanically shaken for 30 minutes, and centrifuged (with the supernatant and the residue being retained and washed, respectively). The residue was transferred (with double-distilled water) to a clean polypropylene beaker and oven dried.

5. *Cadmium in the residual phase (including that in crystalline oxides):* the residue from step 4 was digested in a mixture containing 8 ml of hydrofluoric acid and 3 ml of nitric acid. This method was slightly different from that prescribed by Tessier *et al.* (1979); however, the overall effect—dissolution of any remaining mineral matter—was the same.

Many of the samples were sequentially extracted in duplicate. Supernatant solutions and the digestion extracts obtained in step 5 were analysed for cadmium either by FAAS or GFAAS, depending on their range of cadmium concentrations. In the cases of steps 1–4 these analyses were carried out during the course of the sequential extraction.

The method of standard additions revealed that no significant (>4%) interferences were present in the FAAS analyses of cadmium. However, substantial (≈90%) suppression of cadmium's atomic absorption signal was initially observed in the GFAAS analysis of extracts from step 1 (which contained magnesium chloride), a problem which was overcome by addition to the graphite furnace of 2 µl of 4 M AR phosphoric acid with each sample (Stewart, 1989). (Mubarak *et al.* (1978) has previously noted that magnesium ions tend to lower the cadmium adsorption signal in GFAAS, irrespective of the associated anion.) No further significant interferences to the GFAAS analyses of cadmium in sequential extraction extracts were detected. Other parameters used in the GFAAS and FAAS analyses of cadmium in this study are as described in section 3·2·2 and Chapter 14.

Six samples of the certified-reference sediment sample SDN1/2 (International Atomic Energy Agency, Vienna) were digested (using the method outlined in step 5 of the sequential extraction scheme) and analysed for cadmium, in order to obtain an estimate of analytical bias. These samples were found to contain (10.5 ± 0.6) µgCd g^{-1}, a figure which compared well with the certified value of 11 µgCd g^{-1}.

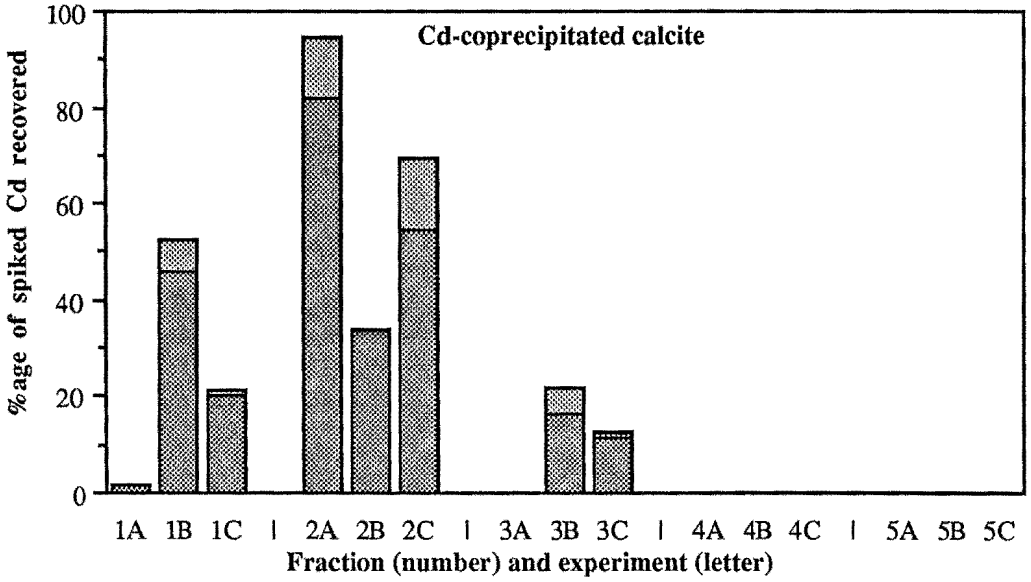
12·3 Results and discussion

12·3·1 Suitability of the sequential extraction for determining the speciations of cadmium in soil

Results relating to the sequential extraction of cadmium-spiked individual phases, synthetic soil mixtures, and Tai Tapu silt loam samples are listed in Appendices 12·2–12·4. Cadmium's phase-distributions in these materials as indicated by sequential extraction are graphed as percentages of the original spiked amounts in Figure 12·1.

Figure 12·1

Phase-distributions of cadmium in cadmium-spiked phases, synthetic soils and Tai Tapu silt loam as determined by sequential extraction. Notes: (a) titles of graphs refer to the cadmium-spiked phase; (b) experiments designated A, B and C are the sequential extractions of the cadmium-spiked phase concerned, the synthetic soil containing that phase, and Tai Tapu silt loam spiked with that phase, respectively; (c) fraction numbers are as defined in section 12·2·3; (d) quantities less than the detection limit are graphed as zero; (e) regions of overlap relate to duplicate determinations.



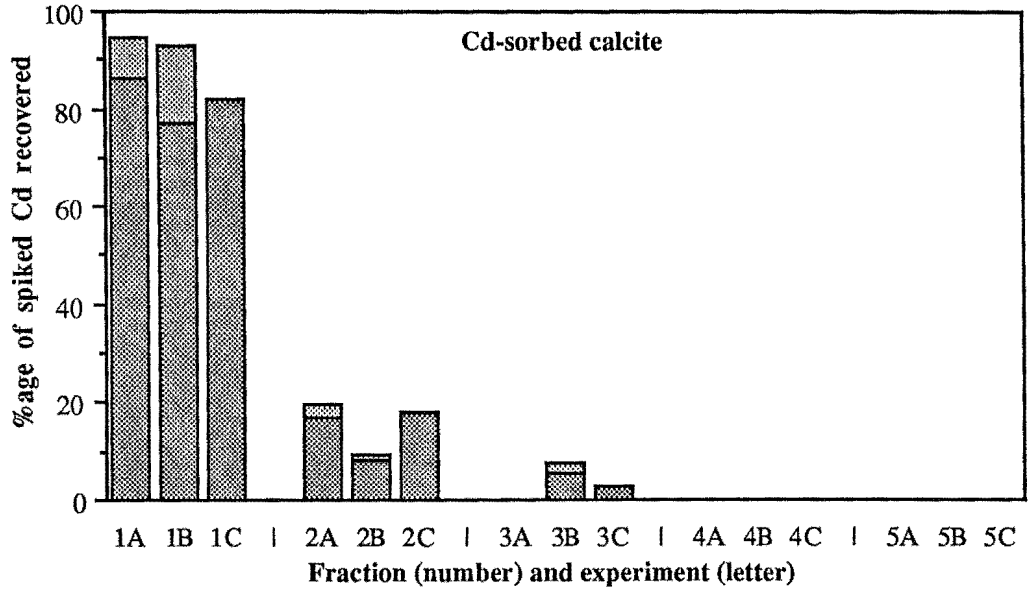
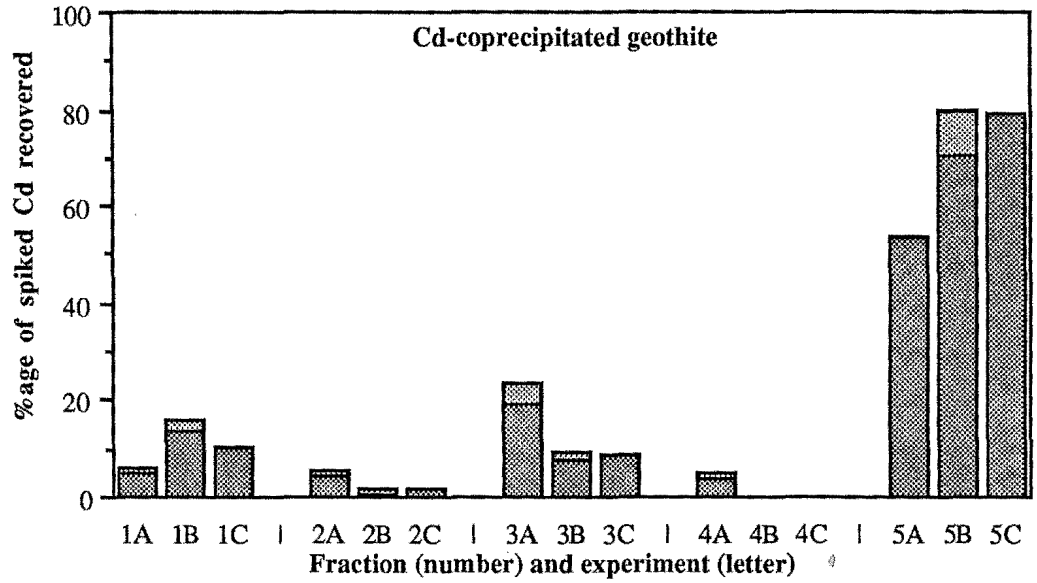


Figure 12·1 continued...



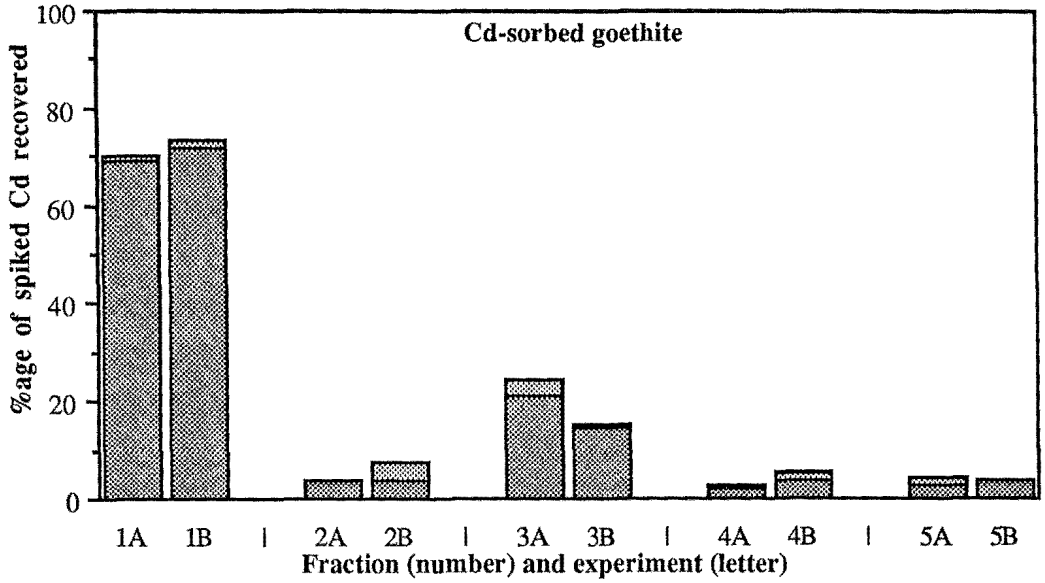
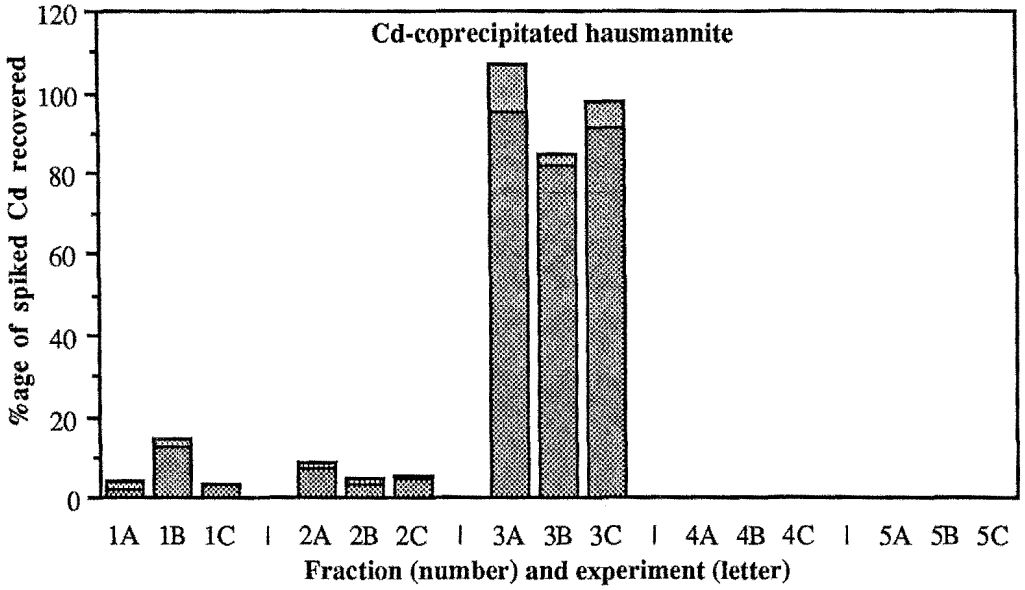


Figure 12·1 continued...



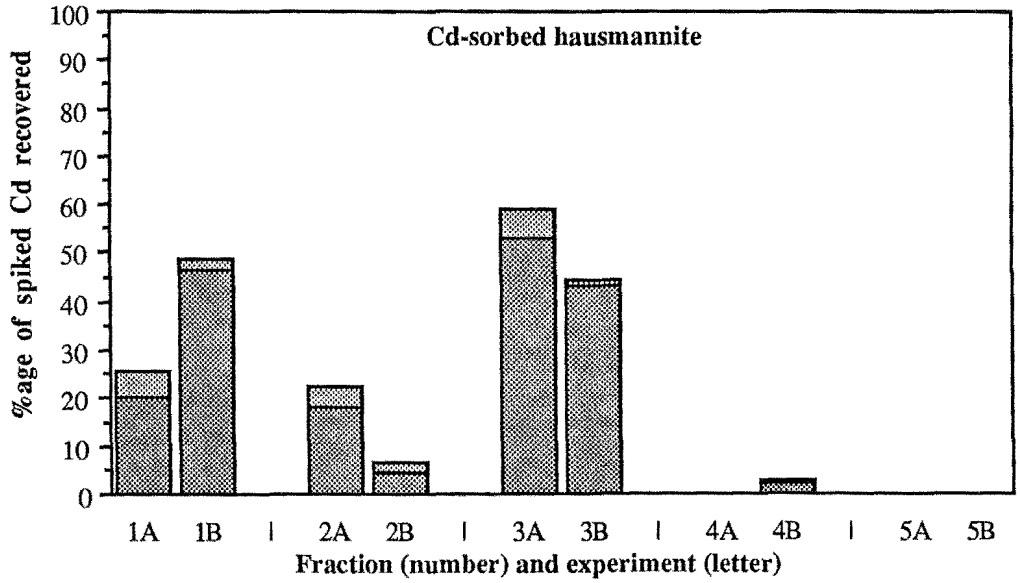
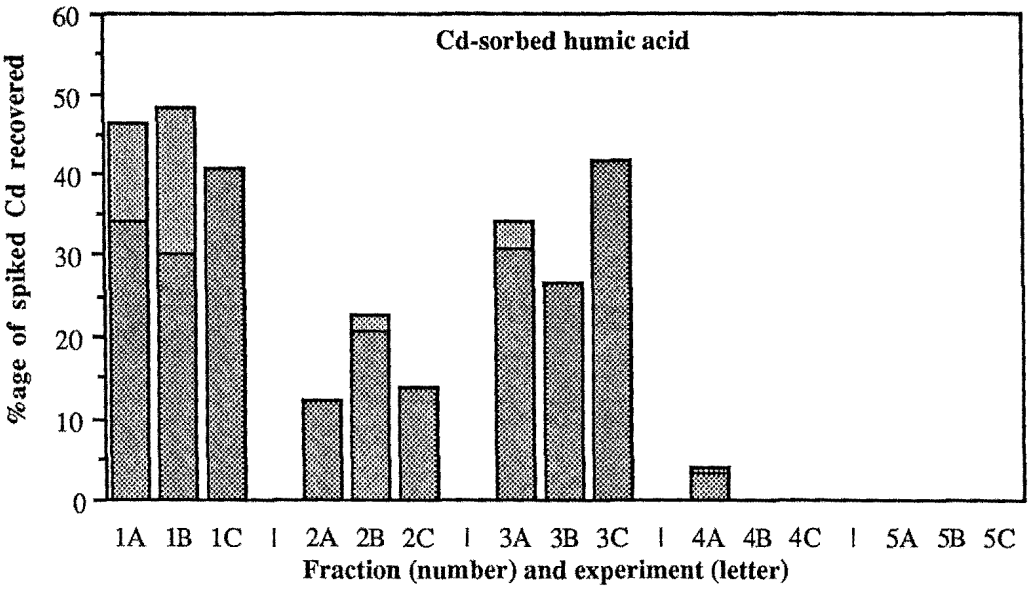
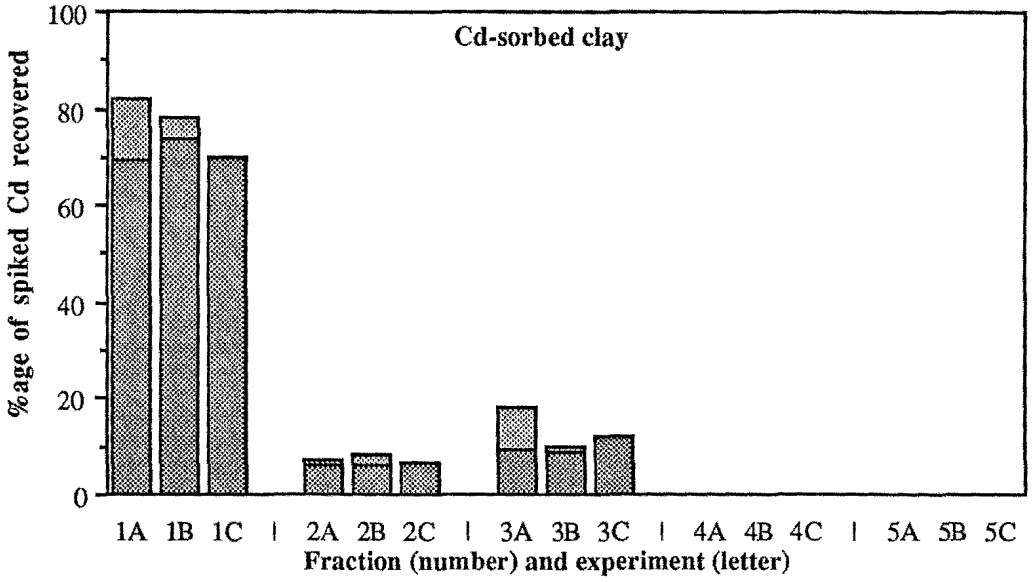


Figure 12·1 continued...





Recoveries of cadmium in the 40 determinations illustrated in Figure 12·1 ranged from 77.2% to 117% (Appendices 12·2–12·4), and the mean cadmium recovery was 97.8% (standard deviation 8.5%). The error associated with each recovery is the sum of the individual errors over the five steps of the sequential extraction, and was estimated to be approximately ±20%.

All sequential extractions of the individual cadmium-spiked phases and of the synthetic soils, and two sequential extractions of the cadmium-spiked Tai Tapu silt loam (relating to cadmium-coprecipitated calcite and hausmannite), were carried out in duplicate. In general, there was good agreement between duplicate determinations of cadmium's phase-distributions in various substances by sequential extraction (Figure 12·1). The overall mean of the coefficients of variation (100 x standard deviation / mean) for those cases where the amount of cadmium in a particular fraction exceeded 10% of the original (spiked) amount was only 8.5%.

The following observations can be made about the sequential extractions of the individual cadmium-spiked phases (1A, 2A, 3A, 4A and 5A in Figure 12·1). (As there was no opportunity for redistribution of cadmium among phases during this part of the study, these findings relate to reagent specificity only.)

1. Most (≈90%) of the cadmium in the cadmium-sorbed calcite was released during step 1 of the sequential extraction scheme ("exchangeable cadmium"), and the remaining cadmium associated with this phase was removed during step 2 ("cadmium bound to carbonates"). Conversely, very little (<2%) of the spiked cadmium was liberated from the cadmium-coprecipitated calcite in step 1 of the sequential extraction scheme, but about 90% of it was released during step 2 (Figure 12·1 and Appendix 12·2). Thus, the extractants used exhibit a good selectivity between cadmium sorbed onto calcite, and cadmium coprecipitated into calcite.
2. A similar statement concerning reagent selectivity can be made in the case of goethite—most of the cadmium associated with the cadmium-sorbed goethite was liberated within the first step of the sequential extraction (and would thus be designated "exchangeable") whereas most of that incorporated into the crystalline goethite was not liberated until the final step ("residual material including crystalline oxides") (Figure 12·1). Interestingly, moderately high (≈23%) amounts of cadmium were liberated from both cadmium-sorbed goethite and cadmium-coprecipitated goethite during step 3 of the scheme, designed to dissolve (among other things) amorphous iron oxides. There could be several reasons for this, among which are that (a) a portion of the cadmium-coprecipitated goethite may have been amorphous, and (b) the increase in acidity in moving from step 2 (pH 5.0) to step 3 (about pH 2) may have been sufficient to cause the release of "stubborn" specifically adsorbed cadmium from high-energy sites on the surface of the cadmium-sorbed goethite. Additionally, a small amount (about 3%) of the cadmium associated with the cadmium-sorbed goethite was detected in the residual phase, suggesting that some

cadmium may have become incorporated within goethite's crystalline lattice during the preparation of the sorbed phases.

3. Almost all (>95%) of the cadmium in the cadmium-coprecipitated hausmannite was released during step 3 of the sequential extraction scheme ("easily reducible manganese oxides and amorphous iron oxides"), indicating a good selectivity of the reagents for this phase (Figure 12·1). About 43% of the cadmium associated with the cadmium-sorbed hausmannite was liberated within the first two steps (which it was expected would release exchangeable, other adsorbed and carbonate-bound cadmium), and about 56% of the cadmium in this phase was not released until step 3. In terms of extractant selectivity for cadmium-sorbed hausmannite, this result is somewhat ambiguous, because it is possible that significant amounts of cadmium may have been incorporated into the crystalline lattice of the hausmannite during the preparation of sorbed phases.
4. Most (≈88%) of the cadmium adsorbed by the clay was liberated during step 1 of the sequential extraction (Figure 12·1). Remaining cadmium in this phase was released during steps 2 and 3, probably as a result of increasing acidity (pH 5.0 for step 2 and pH 2.0 for step 3). Cadmium released from the clay during step 3 (≈9%) could represent that which had been adsorbed by "cadmium-specific" high-energy sites on the clay surface (Chapter 10). If this was the case, it is possible that cadmium formerly adsorbed by high-energy sites on the soil's clay fraction could account for a portion of the cadmium designated as being "associated with easily reducible manganese oxides and amorphous iron oxides" in the sequential extraction of some environmental soil samples.
5. About 50% of the cadmium associated with the cadmium-sorbed humic acid was liberated during the first two steps of the sequential extraction scheme, which were the appropriate steps for adsorbed cadmium to be released (Figure 12·1 and Appendix 12·2). However, about 33% of the cadmium associated with this phase was released during step 3 (as with the clay, this may have represented strongly sorbed cadmium), and a small amount (about 3.5%) of the cadmium was released during step 4, which was specifically designed to oxidise organic matter (Tessier *et al.* 1979). In the cases of some soils, this behaviour could easily result in significant overestimates of the importance of manganese oxides and amorphous iron oxides, and underestimates of the importance of organic matter, in determining (for example) the extent of cadmium adsorption.

A certain amount of confusion is likely to arise from the classification system used in the sequential extraction. For example, cadmium released from the cadmium-sorbed humic acid during steps 1–3 was all, to varying degrees, "bound" to the humic acid, but would not be classified as "bound to organic matter" under the sequential extraction scheme. Rather, half of it would be (correctly) designated "exchangeable and adsorbed and/or carbonate bound" and one-third of it would be (incorrectly) classified as "bound to amorphous iron oxides and easily reducible manganese oxides", but only about 4% of it would be designated

"bound to organic matter." In other words, the designation of cadmium liberated in the extract of step 4 as "bound to organic matter" tends to imply that cadmium in the first three extracts was not that which had been bound to organic matter, when in fact it was.

The same comment can be made about cadmium-sorbed calcite, goethite and hausmannite. If, for example, all of the cadmium associated with the amorphous iron and manganese oxide fraction of a given soil sample was present in an adsorbed form, most of it would probably be removed within the first two steps of a sequential extraction, and thus be designated (correctly) "exchangeable" and "carbonate bound and/or adsorbed", and not "bound to amorphous iron oxides and easily reducible manganese oxides". This particular misinterpretation problem could be quite serious, as adsorption is thought to be the principal means by which amorphous iron oxides and manganese oxides sequester cadmium (Greenland and Hayes, 1978; Reid and McDuffie, 1981).

Cadmium phase-distributions of the cadmium-spiked synthetic soils and Tai Tapu silt loam samples are illustrated in Figure 12·1 (1B–5B and 1C–5C, respectively). Surprisingly, these distributions are very similar to those relating to the individual cadmium-spiked phases, and reveal minimal cadmium redistribution. The main discrepancies evident are those relating to the phase-distributions of cadmium-sorbed calcite, cadmium-coprecipitated calcite and cadmium-sorbed hausmannite spiked into the synthetic soils and Tai Tapu silt loam samples; these are discussed below.

In the sequential extraction of the (individual) cadmium-coprecipitated calcite, about 2%, 88% and 0% of the introduced cadmium was released during steps 1, 2 and 3 (respectively); whereas in the case of the synthetic soil containing cadmium-coprecipitated calcite, the amounts of cadmium released during steps 1, 2 and 3 were 49%, 34% and 19% (respectively) (Appendices 12·2–12·4 and Figure 12·1). In terms of steps 1 and 2, differences in these phase-distributions can be rationalized on the basis of the acidities of the substrates involved (they are not "true" redistributions involving adsorption, as they occurred in the wrong order). The pH of 0.025 g of calcite in 8 ml of double-distilled water was 7.67, whereas that of 0.5 g of the synthetic soil in 8 ml of double-distilled water was 6.00 (these proportions were the same as those used in the first step of the sequential extraction). The higher acidity of the synthetic soil was probably due to the presence of humic acid (pH 2.33), and it would seem reasonable to assume that it may have caused proportionately more of the calcite to dissolve during step 1 of the sequential extraction. Weight is lent to this theory by the fact that both the pH of the Tai Tapu silt loam spiked with cadmium-coprecipitated calcite (6.40), and the amounts of cadmium extracted from this material during steps 1 and 2 of the sequential extraction scheme, were intermediate in value between the pH values of and amounts of cadmium extracted from the other two materials containing cadmium-coprecipitated calcite.

Thus, differences in the amounts of cadmium extracted from the cadmium-coprecipitated calcite (alone) and from the synthetic soil and Tai Tapu silt loam spiked with cadmium-coprecipitated calcite during steps 1 and 2 are likely to be artifacts of the experimental method. However, they do reveal an interesting point—namely, that the

proportion of cadmium classified by this sequential extraction scheme as "exchangeable" (step 1) and the amount designated "bound to carbonates" (step 2) can be highly susceptible to the pH of the material extracted.

Small amounts of "true" redistribution do appear to have occurred in the case of the synthetic soil spiked with cadmium-sorbed hausmannite and in the cases of the synthetic soil and the Tai Tapu silt loam samples spiked with both cadmium-contaminated forms of calcite (Figure 12·1). (No experiment was conducted involving cadmium-sorbed hausmannite in Tai Tapu silt loam.)

A mean value of about 10% of the cadmium which had been introduced was liberated from the synthetic soils and Tai Tapu silt loam samples spiked with cadmium-sorbed or cadmium-coprecipitated calcite during step 3 of the sequential extractions, whereas in the sequential extractions of the individual cadmium-spiked calcite samples, all the cadmium was released during steps 1 and 2. Cadmium detected in the step 3 extracts of the synthetic soil and Tai Tapu silt loam samples which contained cadmium-spiked calcite is likely to represent that which had been liberated from the calcite during steps 1 and 2 of the sequential extraction and subsequently adsorbed (before recovery) by other phases. It is evident from the preceding discussion that humic acid and clay are two phases which are capable of strongly adsorbing cadmium.

In the case of the synthetic soil spiked with cadmium-sorbed hausmannite, a very small amount of cadmium (about 3% of that introduced) was detected in the extract from step 4 ("bound to organic matter"). This could represent cadmium which had been liberated by any (or all) of the reagents in steps 1–3 and strongly adsorbed by humic acid before recovery.

Overall, redistributions of cadmium from the contaminated phases to the remaining (undissolved) phases during the course of the sequential extractions were minimal (Figure 12·1). In contrast, Kheboian and Bauer (1987) reported substantial redistributions of copper, lead and zinc in synthetic sediment samples when using the sequential extraction scheme of Tessier *et al.* (1979). One factor which may contribute to cadmium's ability to remain dissolved in the extractant solutions under conditions which would allow copper, lead and zinc to be significantly adsorbed by the remaining phases could be that of the four metals, ionic cadmium is stable over the widest pH–E_h range (Hahne and Kroontje, 1973; Hermann and Neumann-Mahlkau, 1985).

Concentrations of cadmium in environmental samples are often far lower than those used in this study. It is possible that redistribution of cadmium during the sequential extraction of environmental samples might be more pronounced, due to the relationship between the metal ion concentration and adsorption (section 10·1·1).

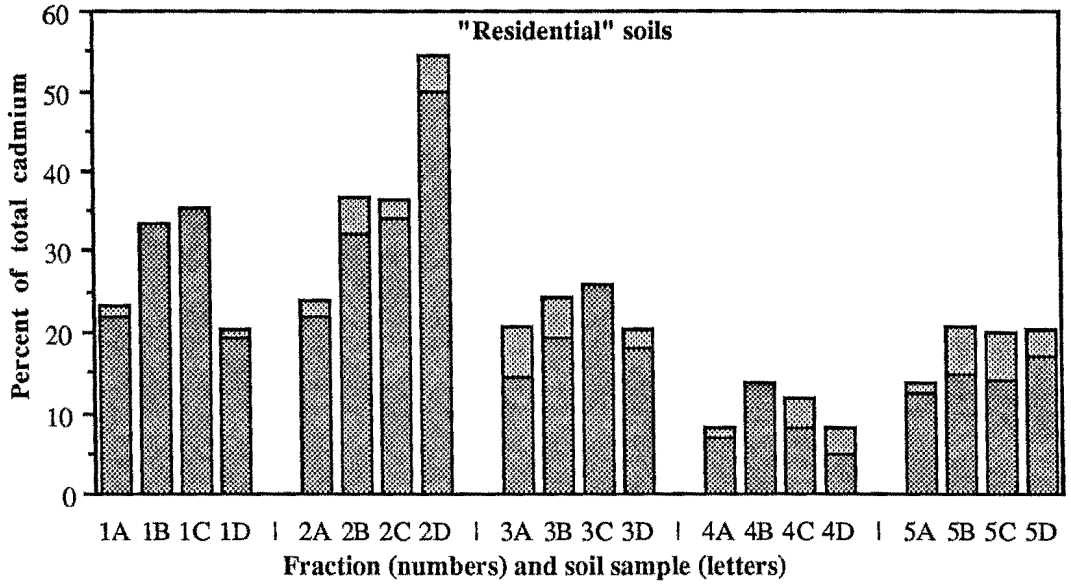
12·3·2 Speciations of cadmium in residential soils, house-dust and road-dust as determined by sequential extraction

Results relating to the sequential extraction of samples of residential soil, road-dust and house-dust are listed in Appendices 12·5–12·7 (respectively). The phase-distributions of

cadmium in these samples as indicated by sequential extraction are graphed as percentages of the original spiked amounts in Figure 12·2 (residential soils and house-dusts) and Figure 12·3 (road-dusts).

Figure 12·2

Phase-distributions of cadmium in samples of residential soil and house-dust as determined by sequential extraction. Notes: (a) experiments designated A–D refer to different samples of the same material (b) fraction numbers are as defined in section 12·2·3; (c) quantities less than the detection limit are graphed as zero; (d) regions of overlap relate to duplicate determinations.



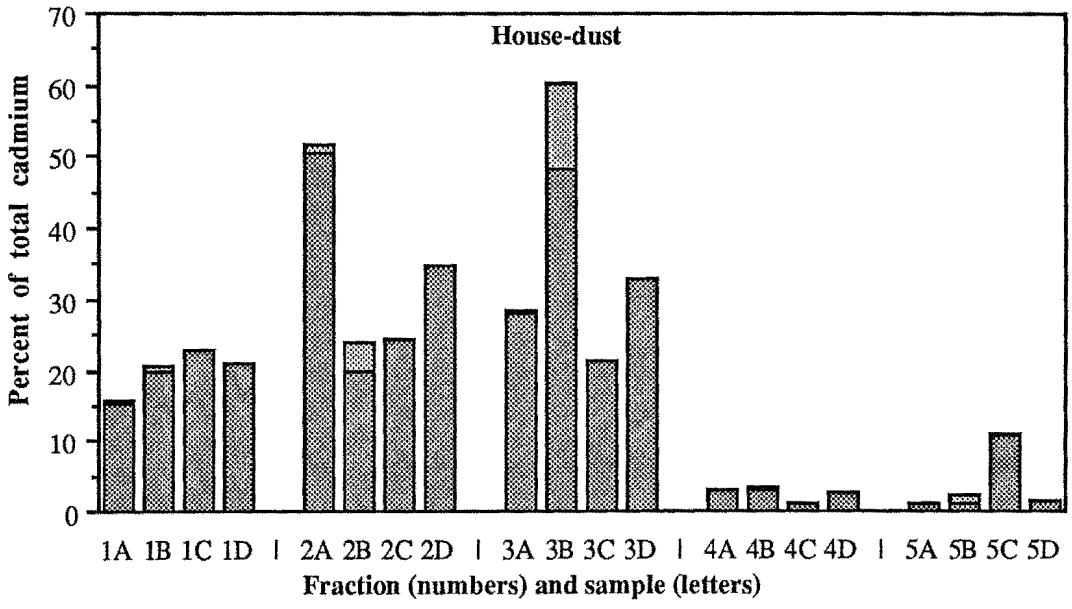


Figure 12·3

Phase-distributions of cadmium in samples of "industrial" road-dust as determined by sequential extraction.
Notes: (a) fraction numbers are as defined in section 12·2·3; (b) quantities less than the detection limit are graphed as zero; (c) regions of overlap relate to duplicate determinations.

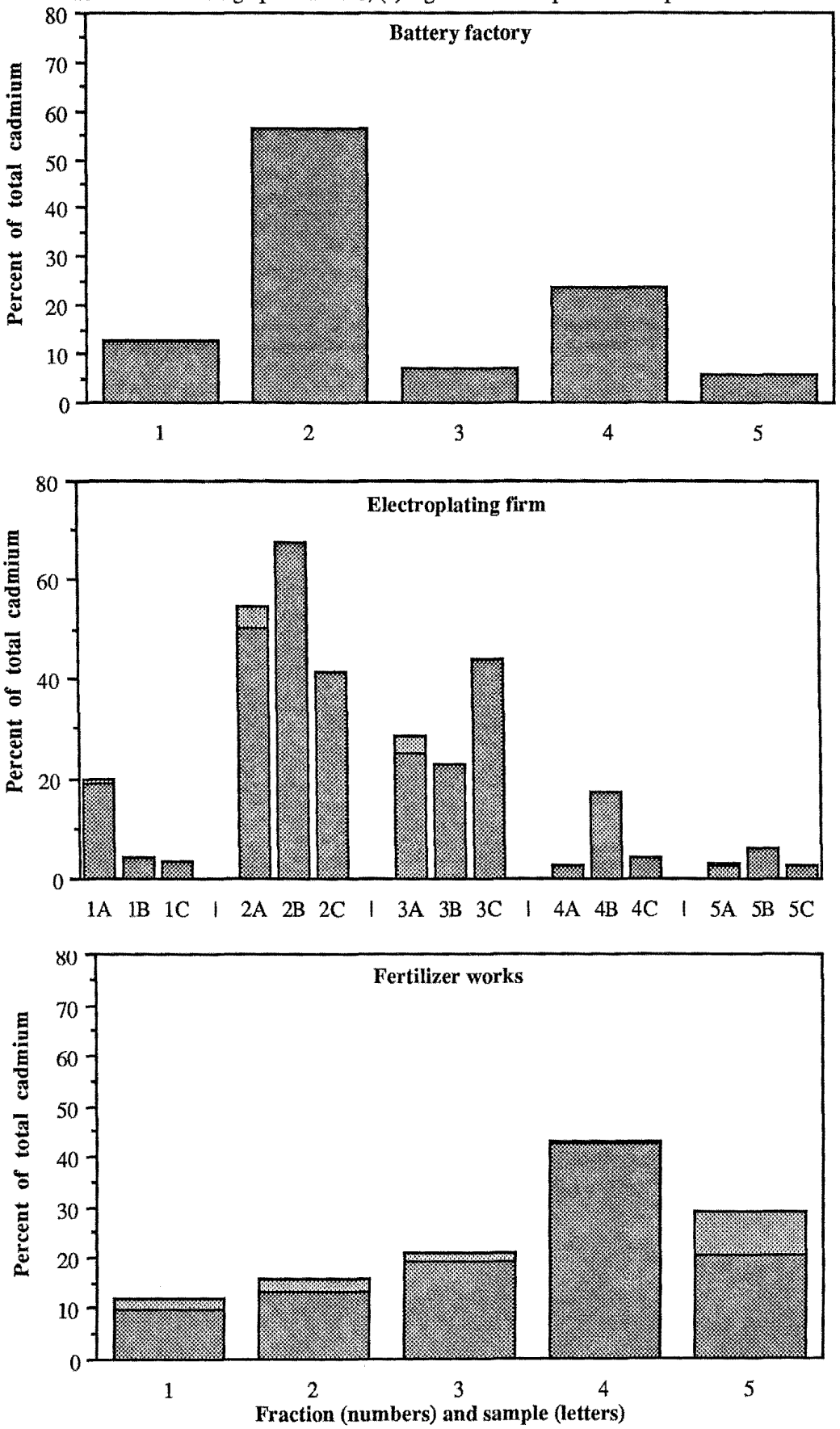
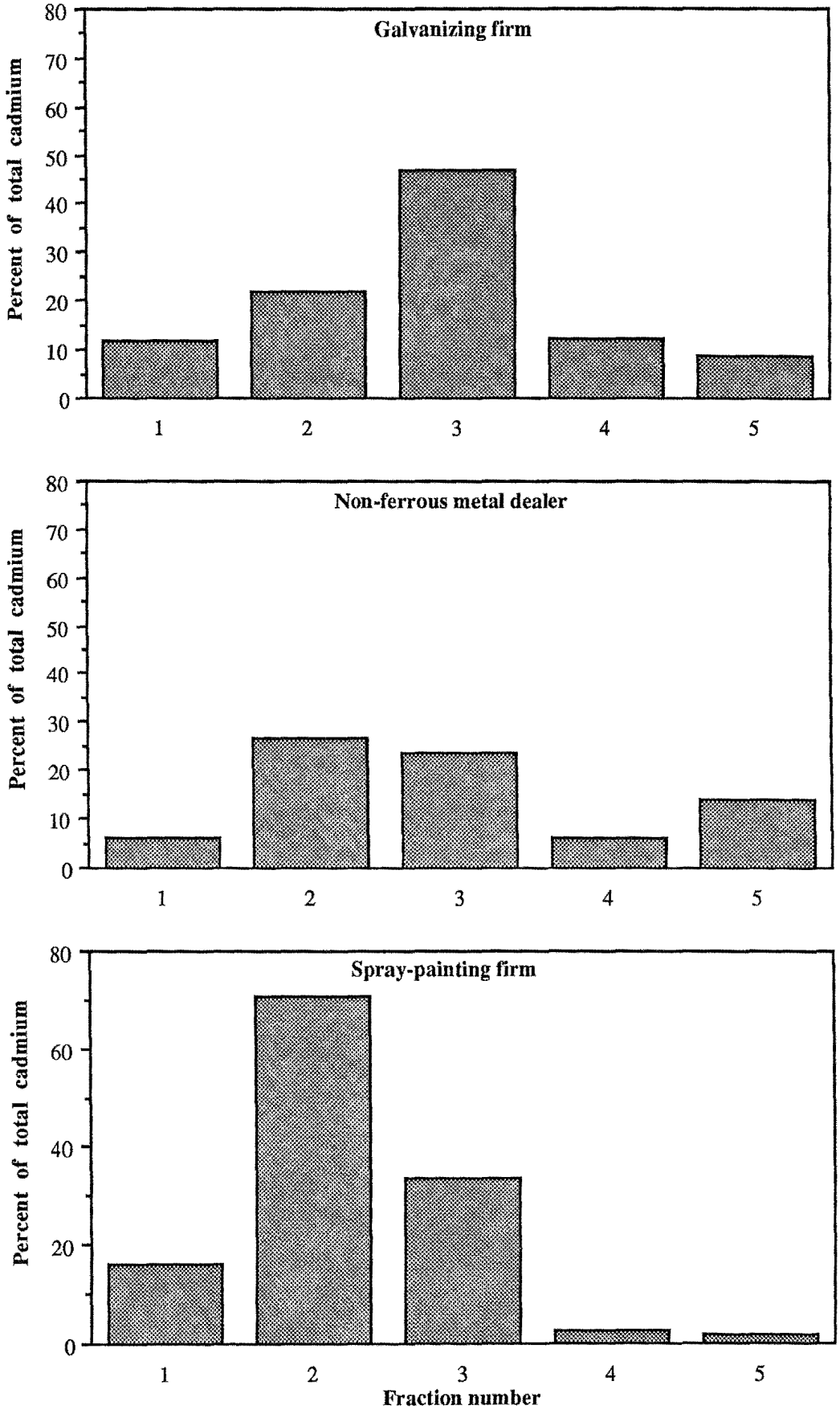


Figure 12·3 continued...



Total concentrations of cadmium in the four residential soil samples were low (with a mean value of 0.110 μgCd g^{-1}) whereas concentrations in the house-dust and road-dust samples were moderately high (with mean values of 5.64 μgCd g^{-1} and 11.0 μgCd g^{-1}, respectively) (Appendices 12·5–12·7). The cadmium phase-distributions of the four residential soil samples (as determined by sequential extraction) are similar, as are those of the four house-dust samples (Figure 12·2). Cadmium phase-distributions in the industrial road-dust samples are more dissimilar (Figure 12·3). Mean values of the percent of total cadmium extracted in each step during the sequential extractions of the residential soil, house-dust and road-dust samples are given in Table 12·3.

Table 12·3

Means, standard deviations and errors on the means for the percentages of cadmium in each sequentially extracted fraction of the residential soil, house-dust and road-dust samples.

Sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Residential soils						
Mean	27.8	35.9	21.1	9.9	15.9	109
Standard devn	7.1	11.4	4.0	3.4	3.1	17
95% error[a]	±5.1	±8.2	±2.9	±2.4	±2.2	±12
House-dusts						
Mean	19.3	34.2	36.6	2.7	3.0	95.8
Standard devn	3.1	14.0	14.7	0.8	3.8	9.7
95% error[a]	±2.8	±12.6	±13.2	±0.7	±3.4	±8.7
Industrial road-dusts						
Mean	11.5	41.9	27.0	15.7	9.4	95.6
Standard devn	5.7	21.3	11.8	15.9	9.1	27.0
95% error[a]	±3.5	±13.0	±7.2	±9.7	±5.6	±16.4
Other studies on road-dust[b]						
Christchurch[d]						
Mean	17.7	31.4	38.3	7.8	4.7	
United Kingdom[c]						
Mean	20	38	28	8	6	

Note: **a.** Student's t-test error on mean.
b. Using the same sequential extraction scheme.
c. Harrison *et al.* 1981.
d. Fergusson and Ryan, 1984.

Most (about 80–90%) of the cadmium in the residential soil and house-dust samples was associated with the first three fractions of the sequential extraction scheme: *i.e.* "exchangeable cadmium", "cadmium bound to carbonates and/or adsorbed cadmium" and "cadmium bound to (easily reducible) manganese oxides and amorphous iron oxides" (Table 12·3 and Figure 12·2).

However, it is evident from the discussion in section 12·3·1 that cadmium extracted in the third fraction could also represent that which had been strongly adsorbed by various

phases. Furthermore, the fact that comparatively low levels of cadmium were extracted in fraction 4—"cadmium bound to organic matter (and/or other oxidisable species)"—does not necessarily imply that little cadmium was "bound to" organic material in the original samples, because cadmium which had been adsorbed by organic matter to varying degrees may well have been removed during steps 1–3 (section 12·3·1).

Notwithstanding these limitations, the five steps of the sequential extraction scheme could be taken to represent the effects of progressively more stringent environmental conditions on cadmium's availability and ease of mobilization in the samples studied. For example, it might be expected that a significant portion of the cadmium released from a given sample during step 2 of the sequential extraction would also be mobilized if, under environmental conditions, the pH of the rainfall fell below 5.0 (which was the pH of the extractant used in step 2 for the dissolution of carbonates).

Proportionately less cadmium (≈3%) was associated with the "residual" phase (step 5) of the house-dust samples than was associated with that phase in the residential soil samples (≈16%) (Table 12·3). This suggests that anthropogenic additions of cadmium to house-dust are likely to be in forms represented by fractions 1–3 (or convert to those forms after addition), and/or that selective enrichment processes for cadmium in house-dust tend to favour those forms (Chapter 4).

The mean phase-distribution of cadmium in the industrial road-dust samples is similar to cadmium phase-distributions in road-dusts which have been reported by other workers who used the same sequential extraction method (Table 12·3; Fergusson and Ryan, 1984; Harrison *et al.* 1981). Overall, the first three fractions accounted for about 80% of the cadmium. Of the five fractions, the greatest proportion of total cadmium was found in the second fraction of samples collected from near the battery factory, electroplating firm, spray painting firm, and non-ferrous metal dealer, in the third fraction of the sample gathered from near the galvanizing firm, and in the fourth fraction in the sample collected from near the fertilizer works. Comments made above regarding cadmium extracted during steps 1–3 of the sequential extraction from residential soil and house-dust samples would also apply to these samples. In this respect, the only road-dust sample worthy of further discussion is that collected from near the fertilizer works, which was unusual in that the fourth and fifth fractions represented substantial portions of the total cadmium content (43% and 25%, respectively) (Appendix 12·6). Cadmium in the fourth fraction could be defined as "strongly bound to organic matter and/or associated with other oxidisable materials", whereas that in the fifth fraction was presumably incorporated into resistant crystalline minerals (section 12·3·1; Kheboian and Bauer, 1987; Tessier *et al.* 1979). It is possible that cadmium-containing sulphides and phosphate rock materials could account for significant amounts of the cadmium liberated from this sample in the fourth and fifth steps (respectively) of the sequential extraction, as the firm involved deals in the manufacture of superphosphate fertilizers (section 3·3·3).

The results of size–density fractionations of industrial road-dust samples collected from the same locations as the road-dust samples sequentially extracted in this part of the study have been given in section 3·3·3.

12·4 Conclusion

Cadmium-spiked "soil phases" were prepared and sequentially extracted using the method of Tessier *et al.* (1979). Reagent selectivity was good in the cases of the three cadmium coprecipitated phases (calcite, goethite and hausmannite). Of the cadmium-sorbed phases, extractant selectivity was high in the cases of calcite and goethite, reasonable in the case of clay, poor in the case of humic acid, and not determined in the case of hausmannite.

The main shortcoming identified in reagent selectivity during sequential extractions was that a portion of the cadmium adsorbed on humic acid (especially) and clay could apparently remain associated with those substrates until step 3 of the sequential extraction scheme. Release during this step would could lead to the incorrect classification of the formerly adsorbed cadmium as "bound to easily reducible manganese oxides and/or amorphous iron oxides."

Another problem identified was that the designations of fractions 2–4 as "bound to carbonates and/or adsorbed", "bound to easily reducible manganese oxides and amorphous iron oxides" and "bound to organic matter" tended to imply that these fractions contained most or all of the cadmium associated with carbonates, manganese oxides and amorphous iron oxides, and organic matter (respectively), which was untrue in the cases of the cadmium-sorbed phases studied.

Sequential extractions of cadmium-spiked synthetic soils and Tai Tapu silt loam samples revealed that little true redistribution of cadmium (from the contaminated phase to the remaining phases) was occurring during the course of the sequential extractions. (It is possible that more "true" redistribution would occur at lower cadmium concentrations.) However, in some cases the pH of the material extracted was found to have a marked effect on the relative proportions of cadmium liberated during step 1 ("exchangeable") and step 2 ("bound to carbonates and/or adsorbed)" of the sequential extraction scheme.

Assuming that the sequential extraction behaviours of the calcite, goethite, hausmannite and humic acid used in this study are reasonably close to those shown by carbonates, iron oxides, manganese oxides and organic matter (respectively) in real soils, the five fractions of the sequential extraction scheme of Tessier *et al.* (1979) could be reclassified for cadmium as follows:

Fraction 1: Weakly adsorbed (to any of the species in listed in steps 2–4 or to other phases);

Fraction 2: Adsorbed (to the species in steps 3 and 4 or other phases) and/or carbonate bound;

Fraction 3: Strongly adsorbed to organic matter and/or strongly bound to (easily reducible) manganese oxides and amorphous iron oxides;

Fraction 4: Very strongly bound to (or incorporated into) organic matter or other oxidisable species;

Fraction 5: Incorporated within resistant minerals.

Most (about 80–90%) of the cadmium in the residential soil, industrial road-dust and house-dust samples was associated with the first three fractions of the sequential extraction scheme.

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12·6 Appendices

Appendix 12·1 (section 12·2·1)

Comparison of d-spacings (Å) and relative intensities (subscripts) of calcite, goethite and hausmannite prepared in this study with values given in the literature[a].

	Pattern listed in literature	Pattern of compound prepared in this study	
		Clean	Cd-coprecipitated
Calcite			
	3.86_{12}	3.85_{6}	3.85_{4}
	3.04_{100}	3.03_{100}	3.03_{100}
	2.85_{2}	2.84_{2}	2.84_{1}
	2.50_{15}	2.49_{29}	2.49_{28}
	2.29_{28}	2.28_{13}	2.28_{28}
	2.10_{18}	2.09_{11}	2.09_{7}
	1.93_{5}	1.93_{3}	1.93_{1}
	1.91_{17}	1.91_{14}	1.91_{11}
	1.87_{17}	1.87_{13}	1.87_{9}
	1.63_{4}	1.63_{2}	1.63_{1}
	1.60_{8}	1.60_{4}	1.60_{1}
	1.592		
	1.53_{5}		
	1.52_{4}	1.52_{3}	1.52_{3}
	1.51_{3}	1.51_{1}	1.51_{1}
	1.47_{2}		
	1.44_{5}	1.44_{1}	1.44_{1}
	1.42_{3}	1.42_{1}	1.421

Appendix 12·1 continued...

	Pattern listed in literature	Pattern of compound prepared in this study	
		Clean	Cd-coprecipitated
Goethite			
	4.98_{10}	4.98_{18}	4.98_{15}
	4.18_{100}	4.18_{100}	4.18_{100}
	3.38_{10}	3.38_{15}	3.38_{15}
	2.69_{30}	2.69_{45}	2.69_{42}
	2.52_{4}		
	2.49_{16}	2.49_{21}	2.49_{20}
	2.45_{20}	2.45_{64}	2.45_{61}
	2.25_{10}		
	2.19_{20}	2.19_{20}	2.19_{18}
	2.10_{2}		
	1.92_{6}		
	1.80_{8}		
	1.77_{2}		
	1.72_{20}	1.72_{33}	1.72_{30}
	1.69_{10}		
	1.56_{16}	1.56_{20}	1.56_{18}
Hausmannite			
	4.94_{30}	4.94_{32}	4.94_{33}
	3.09_{50}	3.09_{39}	3.09_{37}
	2.89_{30}	2.89_{24}	2.89_{26}
	2.77_{90}	2.77_{82}	2.77_{70}
	2.49_{100}	2.49_{100}	2.49_{100}
	2.36_{40}	2.36_{34}	2.36_{30}
	2.04_{40}	2.04_{32}	2.04_{33}
	1.83_{20}		
	1.80_{50}	1.79_{32}	1.79_{33}
	1.71_{30}	1.71_{18}	1.71_{22}
	1.64_{20}		
	1.58_{50}	1.58_{32}	1.58_{28}
	1.54_{80}	1.54_{50}	1.54_{70}
	1.47_{10}		
	1.45_{40}	1.43_{26}	1.43_{22}

Note: a. Berry, 1972. PDF numbers 5–586 (calcite) , 17–536 (goethite) and 16–154 (hausmannite).

Appendix 12·2 (section 12·3·1)

Distributions of cadmium as determined by sequential extraction of the individual cadmium-spiked phases. (Classifications of the extracted fractions are given in section 12·2·3.)

	Cadmium concentration ($\mu g\ g^{-1}$)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Run # 1							
Calcite (C)	49.7	0.72	47.0	<0.1	<0.4	<0.3	47.7
Goethite (C)	29.0	1.76	1.28	6.75	1.40	15.5	26.7
Hausmannite (C)	25.3	0.48	2.14	27.0	<0.4	<0.3	29.6
Humic acid (S)	43.4	20.0	5.22	14.8	1.40	<0.3	41.4
Clay (S)	115	79.6	8.00	10.5	<0.4	<0.3	98.1
Calcite (S)	30.5	28.8	6.08	<0.1	<0.4	<0.3	34.9
Goethite (S)	79.4	54.6	2.94	19.3	2.25	3.25	82.3
Hausmannite (S)	80.0	20.4	17.9	47.0	<0.4	<0.3	85.3
Run # 2							
Calcite (C)	49.7	0.96	40.8	<0.1	<0.4	<0.3	41.8
Goethite (C)	29.0	1.44	1.60	5.5	1.1	15.6	25.2
Hausmannite (C)	25.3	0.96	1.84	24.0	<0.4	<0.3	26.8
Humic acid (S)	43.4	14.8	5.28	13.4	1.65	<0.3	35.1
Clay (S)	115	94.4	6.64	10.5	<0.4	<0.3	112
Calcite (S)	30.5	26.4	5.20	<0.1	<0.4	<0.3	31.6
Goethite (S)	79.4	55.6	3.04	16.8	1.64	2.0	79.1
Hausmannite (S)	80.0	16.0	14.4	42.5	<0.4	<0.3	72.9

	Percent of spiked cadmium (%)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Run # 1							
Calcite (C)	100	1.4	94.6	<0.2	<0.8	<0.6	96.0
Goethite (C)	100	6.1	4.4	23.3	4.8	53.4	92.0
Hausmannite (C)	100	1.9	8.5	107	<1.7	<1.2	117
Humic acid (S)	100	46.1	12.0	34.1	3.2	<0.7	95.4
Clay (S)	100	69.2	7.0	9.1	<0.3	<0.3	85.3
Calcite (S)	100	94.4	19.9	<0.3	<1.2	<0.9	114
Goethite (S)	100	68.8	3.7	24.3	2.8	4.1	104
Hausmannite (S)	100	25.5	22.4	58.8	<0.5	<0.4	107
Run # 2							
Calcite (C)	100	1.9	82.1	<0.2	<0.8	<0.6	84.0
Goethite (C)	100	5.0	5.5	19.0	3.8	53.8	87.1
Hausmannite (C)	100	3.8	7.3	94.9	<1.6	<1.2	106
Humic acid (S)	100	34.1	12.2	30.9	3.8	<0.7	81.0
Clay (S)	100	82.1	5.8	9.1	<0.3	<0.3	97.0
Calcite (S)	100	86.6	17.0	<0.3	<1.2	<0.9	104
Goethite (S)	100	70.0	3.8	21.2	2.1	2.5	99.6
Hausmannite (S)	100	20.0	18.0	53.1	<0.5	<0.4	91.1

Note: a. (S) represents cadmium-sorbed phases and (C) represents cadmium-coprecipitated phases.

Appendix 12·3 (section 12·3·1)

Distributions of cadmium in the "synthetic soils" as determined by sequential extraction. (Classifications of the extracted fractions are given in section 12·2·3.)

	Cadmium concentration ($\mu g\ g^{-1}$)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Run # 1							
Calcite (C)	49.7	26.1	16.9	8.16	<0.6	<0.3	51.2
Goethite (C)	29.0	4.00	0.41	2.27	<0.6	23.2	29.9
Hausmannite (C)	25.3	3.60	0.90	20.7	<0.6	<0.3	25.2
Humic acid (S)	43.4	20.9	9.78	11.5	<0.6	<0.3	42.2
Clay (S)	115	84.9	6.63	9.95	<0.6	<0.3	102
Calcite (S)	30.5	28.3	2.57	1.70	<0.6	<0.3	32.6
Goethite (S)	79.4	56.8	2.88	12.1	4.29	3.12	79.2
Hausmannite (S)	80.0	39.1	5.44	35.5	2.14	<0.3	82.2
Run # 2							
Calcite (C)	49.7	22.9	16.8	10.9	<0.6	<0.3	50.6
Goethite (C)	29.0	4.64	0.22	2.64	<0.6	<0.3	25.7
Hausmannite (C)	25.3	3.20	1.09	21.4	<0.6	<0.3	25.7
Humic acid (S)	43.4	13.0	8.88	11.6	<0.6	<0.3	33.5
Clay (S)	115	89.6	7.20	11.4	<0.6	<0.3	108
Calcite (S)	30.5	23.5	2.88	2.38	<0.6	<0.3	28.8
Goethite (S)	79.4	58.4	5.92	11.6	3.2	3.2	82.3
Hausmannite (S)	80.0	37.3	3.36	34.5	1.7	<0.3	76.9

	Percent of spiked cadmium (%)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Run # 1							
Calcite (C)	100	52.5	34.0	16.4	<1.2	<0.6	103
Goethite (C)	100	13.8	1.4	7.8	<2.0	80.0	103
Hausmannite (C)	100	14.2	3.6	81.8	<2.4	<1.2	99.6
Humic acid (S)	100	48.2	22.5	26.5	<1.3	<0.6	97.2
Clay (S)	100	73.8	5.8	8.7	<0.5	<0.3	88.3
Calcite (S)	100	92.8	8.4	5.6	<2.0	<1.0	107
Goethite (S)	100	71.5	3.6	15.2	5.4	3.9	99.6
Hausmannite (S)	100	48.9	6.8	44.4	2.7	<0.4	103
Run # 2							
Calcite (C)	100	46.1	33.8	21.9	<1.2	<0.6	102
Goethite (C)	100	16.0	0.7	9.1	<2.0	70.7	96.5
Hausmannite (C)	100	12.6	4.3	84.6	<2.4	<1.2	102
Humic acid (S)	100	30.0	20.5	26.7	<1.3	<0.7	77.2
Clay (S)	100	77.9	8.0	9.9	<0.5	<0.3	95.8
Calcite (S)	100	77.0	9.4	7.8	<2.0	<1.0	94.2
Goethite (S)	100	73.6	7.5	14.6	4.0	4.0	104
Hausmannite (S)	100	46.6	4.2	43.1	2.1	<0.4	96.0

Note: **a.** (S) represents cadmium-sorbed phases and (C) represents cadmium-coprecipitated phases.

Appendix 12·4 (section 12·3·1)

Distributions of cadmium as determined by sequential extraction of the cadmium-spiked Tai Tapu silt loam. (Classifications of the extracted fractions are given in section 12·2·3.)

	Cadmium concentration ($\mu g\ g^{-1}$)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Calcite (C)	49.7	10.5	34.4	6.3	<0.3	<0.1	51.2
Calcite (C)	49.7	10.0	27.2	5.6	<0.3	<0.1	42.8
Goethite (C)	29.1	3.08	0.44	2.5	<0.3	23.0	29.0
Hausmannite (C)	25.4	0.80	1.36	23.2	<0.4	<0.4	25.4
Hausmannite (C)	25.4	0.80	1.20	24.8	<0.3	<0.3	26.8
Humic acid (S)	43.5	17.6	6.04	18.1	<0.53	<0.13	41.7
Clay (S)	115	80.0	7.66	14.0	<0.3	<0.1	102
Calcite (S)	30.6	25.0	5.48	0.9	<0.1	<0.3	31.4

	Percent of spiked cadmium (%)						
Cd-spiked phase[a]	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Calcite (C)	100	21.1	69.2	12.7	<0.5	<0.3	103
Calcite (C)	100	20.1	54.7	11.3	<0.5	<0.3	86.1
Goethite (C)	100	10.6	1.5	8.6	<0.9	79.0	99.7
Hausmannite (C)	100	3.1	5.4	91.3	<1.5	<1.5	99.8
Hausmannite (C)	100	3.1	4.7	97.6	<1.0	<1.0	106
Humic acid (S)	100	40.5	13.9	41.6	<1.2	<0.3	96.0
Clay (S)	100	70.0	6.7	12.2	<0.3	<0.1	88.4
Calcite (S)	100	81.7	17.9	2.9	<0.4	<0.8	103

Note: **a.** (S) represents cadmium-sorbed phases and (C) represents cadmium-coprecipitated phases.

Appendix 12·5 (section 12·3·2)

Distributions of cadmium in four "residential soil" samples as determined by sequential extraction. (Classifications of the extracted fractions are given in section 12·2·3.)

	Cadmium concentration ($\mu g\ g^{-1}$)						
Soil site no.	Total[a] initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
1	0.146	0.034	0.032	0.030	0.010	0.020	0.126
1	0.146	0.032	0.035	0.021	0.012	0.018	0.118
2	0.087	0.029	0.028	0.021	0.012	0.018	0.108
2	0.087	0.029	0.032	0.017	0.012	0.013	0.103

Appendix 12·5 continued...

Soil site no.	Total[a] initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
	Cadmium concentration ($\mu g\ g^{-1}$)						
3	0.085	0.030	0.031	0.022	0.007	0.017	0.107
3	0.085	0.030	0.029	0.022	0.010	0.012	0.103
4	0.123	0.025	0.059	0.025	0.006	0.021	0.136
4	0.123	0.024	0.067	0.022	0.010	0.025	0.138
Mean	0.110	0.029	0.039	0.023	0.010	0.018	0.117
Std dev	0.027	0.003	0.015	0.004	0.002	0.004	0.014
Error[b]	±0.037	±0.002	±0.010	±0.003	±0.001	±0.003	±0.010
	Percent of spiked cadmium (%)						
Soil site no.	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
1	100	23.2	21.9	20.5	6.8	13.7	86.3
1	100	21.9	24.0	14.4	8.2	12.3	80.8
2	100	33.3	32.1	24.1	13.8	20.7	124
2	100	33.3	36.8	19.5	13.8	14.9	118
3	100	35.3	34.1	25.9	11.8	14.1	121
3	100	35.3	34.1	25.9	11.8	14.1	121
4	100	20.3	50.0	20.3	4.9	17.1	111
4	100	19.5	54.5	17.9	8.1	20.3	112
Mean	100	27.8	35.9	21.1	9.9	15.9	109
Std dev	0	7.1	11.4	4.0	3.4	3.1	17
Error[b]	0	±5.1	±8.2	±2.9	±2.4	±2.2	±12

Notes: **a.** As determined by separate analysis of the whole sample.
b. Student's t-test error on mean at a 95% confidence level.

Appendix 12·6 (section 12·3·2)

Distributions of cadmium in eight "industrial dust" samples as determined by sequential extraction. (Classifications of the extracted fractions are given in section 12·2·3.)

Description	Total[a] initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
	Cadmium concentration ($\mu g\ g^{-1}$)						
Electroplater[b]	16.8	3.34	8.44	4.77	0.427	0.407	17.4
Electroplater[b]	16.8	3.18	9.20	4.17	0.412	0.492	17.5
Electroplater[c]	19.1	0.820	12.9	4.34	3.32	1.14	22.5
Electroplater[d]	18.1	0.642	7.49	7.97	0.797	0.476	17.4

Appendix 12·6 continued...

Description	Total[a] initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
	Cadmium concentration ($\mu g\ g^{-1}$)						
Fertilizer wks	5.77	0.561	0.769	1.20	2.48	1.18	6.19
Fertilizer wks	5.77	0.699	0.899	1.10	2.45	1.67	6.82
Battery factory	3.45	0.443	1.95	0.242	0.814	0.197	3.65
Spray painter	9.93	1.60	7.05	3.34	0.276	0.174	12.5
Non-ferrous metal dealer	12.2	0.767	3.26	2.86	0.759	1.73	9.4
Galvanizer	2.34	0.277	0.509	1.09	0.284	0.206	2.37
	Percent of spiked cadmium (%)						
Description	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
Electroplater[b]	100	19.9	50.2	28.4	2.5	2.4	103
Electroplater[b]	100	18.9	54.7	24.9	2.5	2.9	104
Electroplater[c]	100	4.3	67.5	22.7	17.4	6.0	118
Electroplater[d]	100	3.5	41.4	44.0	4.4	2.6	95.9
Fertilizer wks	100	9.7	13.3	20.7	43.0	20.5	107
Fertilizer wks	100	12.1	15.6	19.1	42.4	28.9	118
Battery factory	100	12.8	56.5	7.0	23.6	5.7	106
Spray painter	100	16.1	71.0	33.6	2.8	1.7	126
Non-ferrous metal dealer	100	6.3	26.7	23.4	6.2	14.2	77.1
Galvanizer	100	11.8	21.8	46.6	12.1	8.8	101

Notes: **a.** As determined by separate analysis of the whole sample.
b. Location 1 (near Cd-plating section).
c. Location 2 (near corner; 3 m W, 40 m S of Cd-plating section).
d. Location 3 (5 m S of hard-chroming section).

Appendix 12·7 (section 12·3·2)

Distributions of cadmium in four house-dust samples as determined by sequential extraction. (Classifications of the extracted fractions are given in section 12·2·3.) *Sample 1* is the composite house-dust sample (n = 120 houses), and *samples 2–4* are single samples from three Christchurch houses.

	Cadmium concentration ($\mu g\ g^{-1}$)						
Sample number	Total[a] initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
1	8.08	1.28	4.10	2.26	0.234	0.090	7.96
1	8.08	1.24	4.18	2.29	0.254	0.090	8.05
2	4.94	0.985	0.980	2.39	0.167	0.060	4.58
2	4.94	1.02	1.18	2.98	0.155	0.109	5.44
3	4.56	1.05	1.11	0.980	0.054	0.490	3.68
4	4.98	1.05	1.73	1.65	0.125	0.078	4.63
Mean	5.64	1.10	2.21	2.09	0.165	0.153	5.72
Std dev	1.64	0.12	1.51	0.69	0.073	0.166	1.85
Error[b]	±2.22	±0.11	±1.36	±0.62	±0.066	±0.150	±1.67
	Percent of spiked cadmium (%)						
Soil site no.	Total initial	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Recovery
1	100	15.8	50.7	28.0	2.9	1.1	98.5
1	100	15.3	51.7	28.3	3.1	1.1	99.6
2	100	19.9	19.8	48.4	3.4	1.2	92.7
2	100	20.6	23.9	60.3	3.1	2.2	110
3	100	23.0	24.3	21.5	1.2	10.7	80.7
4	100	21.1	34.7	33.1	2.5	1.6	93.0
Mean	100	19.3	34.2	36.6	2.7	3.0	95.8
Std dev	0	3.1	14.0	14.7	0.8	3.8	9.7
Error[b]	0	±2.8	±12.6	±13.2	±0.7	±3.4	±8.7

Notes: **a.** As determined by separate analysis of the whole sample.
b. Student's t-test error on mean at a 95% confidence level.

CHAPTER 13
STUDIES RELATING TO THE WEATHERING OF CADMIUM FROM A CADMIUM-CONTAINING PAINT AND GALVANIZED-IRON

13·1 Introduction

In Chapter 5 it was mentioned that a particular variety of red spray-paint, used for painting cars, contained 31 300 $\mu gCd\ g^{-1}$ (dry weight) (the pigment in this paint was presumably a cadmium thioselenide (section 5·3·2)). It was thought possible that weathering of surfaces finished with cadmium-containing paints could be a significant source of cadmium in the environment. Weathering of galvanized-iron products, implicated as a significant source of zinc in Chapters 3, 4, 7 and 9, could also contribute small amounts of cadmium to the environment, due to the geochemical association of cadmium with zinc (section 1·2·1).

The aim of this study was to examine some of the factors likely to govern the loss of zinc and cadmium from galvanized-iron products and from surfaces finished with cadmium-containing paints under environmental conditions. For simplicity, the experiments conducted in this study will be referred to as *weathering experiments* throughout this chapter.

13·2 Method

13·2·1 Preparation of painted steel and galvanized-iron surfaces

A (29.0 x 57.0) cm sheet of mild steel was lightly sandpapered (on both sides), washed thoroughly with double-distilled water, dried, and spray painted with the cadmium-containing red spray-paint mentioned above. In accordance with instructions printed on the paint can, no primer was applied to the steel prior to spray-painting. The painted steel sheet was then heated to 350 °C for 1 hr (in accordance with the instructions and with the usual practice when painting car bodies) for the purpose of hardening the paint. After cooling, the painted steel sheet was placed under running tap water and lightly scrubbed with a nylon brush (in order to remove any loose paint particles), washed with double-distilled water and dried.

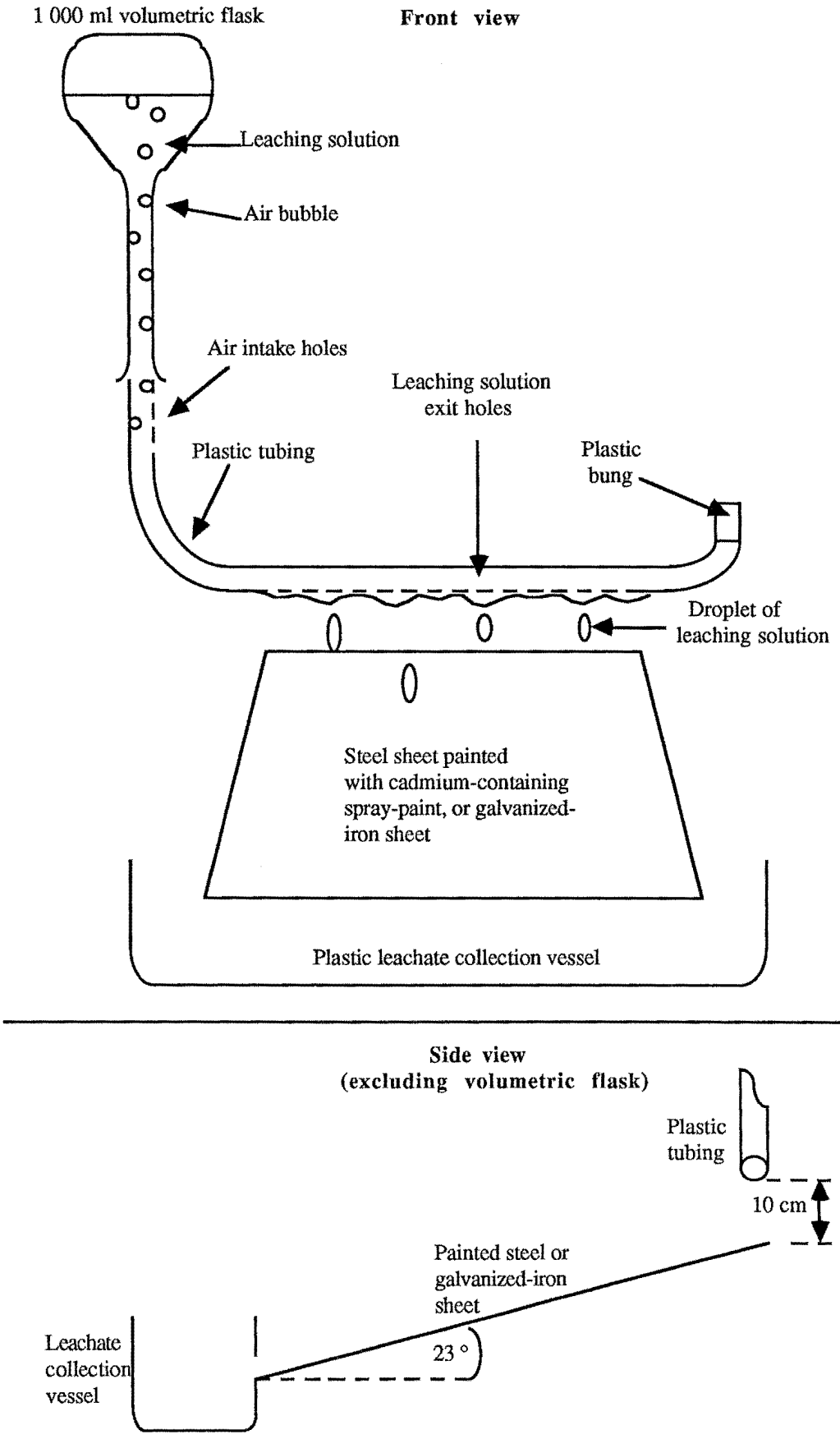
A (27.5 x 44.0) cm sheet of commercially-prepared galvanized-iron was lightly scrubbed with a nylon brush under running tap water, washed with double-distilled water and dried.

13·2·2 Methodology of weathering experiments

A diagram of the apparatus used in all of the weathering experiments is given in Figure 13·1.

Figure 13·1

Diagram of the apparatus used in the weathering experiments.



The apparatus illustrated in Figure 13·1 was designed to simulate rainfall, and it appeared to do this reasonably well. Leaching solution, held in an inverted 1 000 ml volumetric flask, was channelled through plastic tubing, released in the form of droplets from 29 exit holes bored in the plastic tubing (one per centimetre and each of 0.5 mm diameter), and allowed to flow over the upper surface of the galvanized-iron sheet or painted steel sheet (Figure 13·1). Air intake holes were punched in the plastic tubing with a fine pin; the number of these holes could be used to regulate the flow of leaching solution. The total volume of leaching solution used in all experiments was 1 000 ml, and the number of air intake holes was such that 30 minutes was sufficient for most (≈990 ml) of this solution to pass through the exit holes (leaching solution remaining in the plastic tubing after this time was poured directly over the prepared surfaces). The painted steel and galvanized-iron sheets were held at an angle of 23 ° from horizontal, to facilitate runoff of the leaching solution droplets. Most droplets ran over the sheets fairly quickly, typically remaining on their surfaces for 3–7 seconds.

Prior to use, all the plastic and glass components of the apparatus illustrated in Figure 13·1 were soaked in 4 M AR nitric acid, rinsed thoroughly with and then soaked in double-distilled water, and dried.

Weathering experiments relating to the cadmium-containing paint were conducted in a Clean Room (class 100), to minimize the contribution of dust from atmospheric fallout to cadmium concentrations in the leachates. This was not possible in the case of the experiments relating to the galvanized-iron (due to concern about probable zinc contamination of the Clean Room)—these experiments were carried out in a normal laboratory but with a plastic dust-cover placed above the apparatus.

The experiments in this study were primarily designed to measure the effects of *changes* within the weathering system on the amount of cadmium and zinc leached from the cadmium-containing paint and the galvanized-iron (rather than to strictly simulate natural weathering processes). The following parameters were investigated in this respect:

1. Acidity of the leaching solution: AR acetic acid/sodium acetate buffers (0.1 M) were constructed according to the method given in section 10·2·2, and passed through the weathering apparatus in order of decreasing pH. In the case of the painted steel surface, leaching solutions used were of pH 9.0, pH 7.0, pH 5.0, pH 3.0, and pH 1.0, and in the case of the galvanized-iron, they were of pH 9.0, pH 7.0, pH 6.0, pH 5.0, pH 3.0, and pH 1.0. Double-deionised water, of pH 4.1 but with a very low ionic strength (resistivity 14 MΩ), was also used as the leaching solution in some experiments.
2. Ionic strength of the leaching solution: AR acetic acid/sodium acetate buffers, all of pH 5.0 but with varying molarities, were prepared and passed through the weathering apparatus in order of increasing ionic strength. The ionic strengths of the acetic acid/sodium acetate leaching solutions used on the painted steel surface were 0.10, 0.25, 0.50, 1.00 and 2.00, and those of the (acetic acid/sodium acetate) leaching solutions used on the galvanized-iron were 0.05, 0.10, 0.25, 0.50, 1.00 and 2.00.

A range of AR sodium chloride solutions of ionic strength 0.05, 0.10, 0.50, 1.00 and 2.00 were also prepared and passed over the painted steel surface (only), in order to gauge the effect of changing the anion. The pH of these (unbuffered) solutions was found to be (5.1 ± 0.3), allowing comparison between the amount of cadmium lost to sodium chloride leaching solutions and the amount lost to acetic acid/sodium acetate leaching solutions.

3. The combined effect of ultra-violet light and rainwater on the amount of cadmium leached from the cadmium-containing paint, and the effect of rainwater (alone) on the amount of cadmium and zinc leached from the galvanized-iron. After the experiments detailed above, the painted steel surface was irradiated for 6 hours with 5 600 W m^{-2} of ultra-violet light (from a 500 W lamp), and then leached with ten 1 000 ml samples of double-deionised water followed by two further 1 000 ml rainwater samples. Rainwater was collected on various days during April and May 1989 from the roof of the Rutherford Building, University of Canterbury. The amount of ultra-violet radiation experienced by the painted steel surface was later estimated to be equivalent to about 250 sunny days in Los Angeles (Coulson, 1975). The galvanized-iron sheet was not irradiated but was directly leached with two portions of rainwater.

All experiments were conducted at (20 ± 2) °C. Between each set of experiments (1–3 above), the painted steel and galvanized-iron sheets and the plastic leachate collection vessel (Figure 13·1) were washed thoroughly with double-deionised water. After each experiment, two 100 ml samples were taken from the (stirred) leachate, and the remainder was discarded.

An assumption in the methodology outlined above was that each weathering experiment had a negligible effect on the total amount of cadmium and zinc leachable from the two surfaces, and thus did not unduly influence the results of subsequent weathering experiments. Evidence gathered during the course of the experiments (section 13·3) suggested that this assumption was likely to have been true.

13·2·3 Handling and analysis of leachates

Sodium chloride solution leachates were passed through an iminodiacetate chelating resin (in order to isolate divalent cadmium from sodium ions and chloride ions), a process which involved the following steps (Kingston *et al.* 1978; Paulson, 1986):

1. "Chelex 100" resin (6 ml, sodium form) was washed and prepared by passing through it four 5 ml portions of 2.5 M AR nitric acid, two 5 ml portions of double-distilled water, three 5 ml samples of 2.0 M AR ammonium acetate, 15 ml of double-distilled water, and two drops of 8 M AR ammonium acetate solution.
2. The pH of each 100 ml sample of the sodium chloride solution leachate was adjusted to 5.0–5.5 with 2 M AR ammonium hydroxide solution, after which 0.5 ml of 8 M AR ammonium acetate was added (as an aid to buffering the system). The solution was then passed through the prepared resin at the rate of 1 ml min^{-1}.

3. Sodium ions were eluted using four 10 ml portions of 1.0 M ammonium acetate, and residual ammonium acetate was washed away with 20 ml of double-distilled water.
4. 7 ml of 2.5 M nitric acid was added to the resin for the purpose of eluting cadmium.

The solution recovered from step 4 was diluted to 25 ml and analysed for cadmium by GFAAS, using 0.7 M nitric acid as an analytical blank (parameters were as given in section 3·2·2 and Chapter 14). Kingston *et al.* (1978) reported a cadmium-109 recovery of 99.99% from spiked seawater samples by use of the above method.

Acetic acid/sodium acetate solution leachates were analysed for cadmium and zinc by GFAAS and FAAS (respectively), using the parameters given in section 3·2·2 and Chapter 14. These solutions were diluted in cases of high ionic strength, and clean acetic acid/sodium acetate solutions (of the appropriate pH and ionic strength) were used as analytical blanks. (A cadmium absorbance of 0.030 was observed in "clean" 2 M acetic acid/sodium acetate solution.) Double-deionised water and rainwater leachates used on the painted surface were analysed directly (with samples of clean double-deionised water serving as analytical blanks). Leachates of rainwater and double-deionised water which had been used on the galvanized-iron sheet were preconcentrated 20 times by freeze drying (according to the technique described in section 9·2·1) prior to analysis.

Atomic absorption peaks for cadmium were in all cases sharp and symmetrical, and no evidence of significant interferences to cadmium and zinc analyses was revealed by the method of standard additions.

13·3 Results and discussion

13·3·1 Weathering of the cadmium-containing paint

Results of weathering experiments on the cadmium-containing paint are listed in Appendix 13·1. The mean amounts of cadmium lost from this surface with the various leaching solutions used are listed in Table 13·1.

Table 13·1

Mean amounts of cadmium lost from the surface coated with the cadmium-containing paint with each type of leaching solution.

Leaching solution	Amount of cadmium lost from the painted steel (μg)			
	No. of runs	Mean	Standard devn	95% error[a]
Double-deionised water (pH 4.10)				
before UV irradiation of paint	3	0.41	0.06	±0.12
after UV irradiation of paint	10	2.47	0.23	±0.17
Rainwater (pH 4.50)[b]	2	11.3	1.1	±7.1
0.1 M acetic acid/sodium acetate solution (various acidities)	10	2.40	0.80	±0.49

Table 13·1 continued...

Leaching solution	Amount of cadmium lost from the painted steel (μg)			
	Number (n)	Mean	Standard devn	95% error[a]
pH 5.0 acetic acid/sodium acetate solution (various ionic strengths)	9	4.03	1.51	±1.00
sodium chloride solution (various ionic strengths)	5	1.13	0.54	±0.57

Notes: **a.** Student's t-test.
b. After UV irradiation of the paint.

The absolute amounts of cadmium leached from the cadmium-containing paint were low, considering that the paint contained 31 300 μgCd g^{-1} (dry weight); mean amounts of cadmium leached per 1 000 ml of leaching solution ranged from 0.41 to 11.3 μg (Table 13·1). However, the fact that cadmium could be leached from this surface (even with double-deionised water) implies that the weathering of products coated with this paint would result in the release of a certain amount of cadmium to the environment.

The mean annual rainfall experienced by Christchurch over the period 1983–1986 was 638 mm (Anon. 1987). Assuming that the supply of leachable cadmium was not exhausted, it might be expected that the amount of cadmium that would leach from each square metre of a surface covered with this paint using a volume of leaching solution equivalent to the average annual rainfall could range from 260 μg (using double-deionised water before UV irradiation) to 7 180 μg (using rainwater after UV irradiation). Thus, it is possible that in the long term, the weathering of products coated with cadmium-containing paints may result in the release of substantial amounts of cadmium to the environment. (No attempt will be made, by drawing on this data, to quantify the likely contribution made by weathering of cadmium-containing paints to anthropogenic cadmium inputs, due both to the complexity of environmental weathering processes when compared with the experiments carried out in this study, and to the fact that the supply of leachable cadmium from a particular cadmium-containing paint may well be limited.)

The ultra-violet irradiation of the paint caused a sixfold increase in the amount of cadmium leached to double-deionised water (Table 13·1). This could be attributed to a partial breakdown of the paint's organic matrix, an effect which would presumably allow some of the initially occluded cadmium to become available to the leaching solutions. The result implies that in the long term, exposure to sunlight would tend to increase the amount of cadmium leachable from this paint.

Rainwater (pH 4.50) was 4.6 times more efficient at leaching cadmium from the irradiated paint than double-deionised water (pH 4.10), possibly because it was of higher ionic strength.

The amount of cadmium lost from the paint to a given leaching solution (before and after UV irradiation) was fairly constant between experimental runs, and showed little sign of decreasing (Appendix 13·1), implying that each experiment was having a negligible effect on the total amount of leachable cadmium on the paint's surface (section 13·2·2). (The overall mean of the coefficients of variation for the 11 experiments which were repeated was 14%, and individual coefficients of variation ranged from 1% to 34%.)

Relationships between the amount of cadmium leached from the cadmium-containing paint and the pH and ionic strength of the leaching solutions are illustrated in Figures 13·2 and 13·3 (which are derived from the data in Appendix 13·1). Correlation coefficients, probabilities and equations of the relationships graphed in Figures 13·2 and 13·3 are listed in Table 13·2.

Figure 13·2

Effect of acidity of the 0.1 M acetic acid/sodium acetate leaching solutions on the amount of cadmium leached from the painted surface.

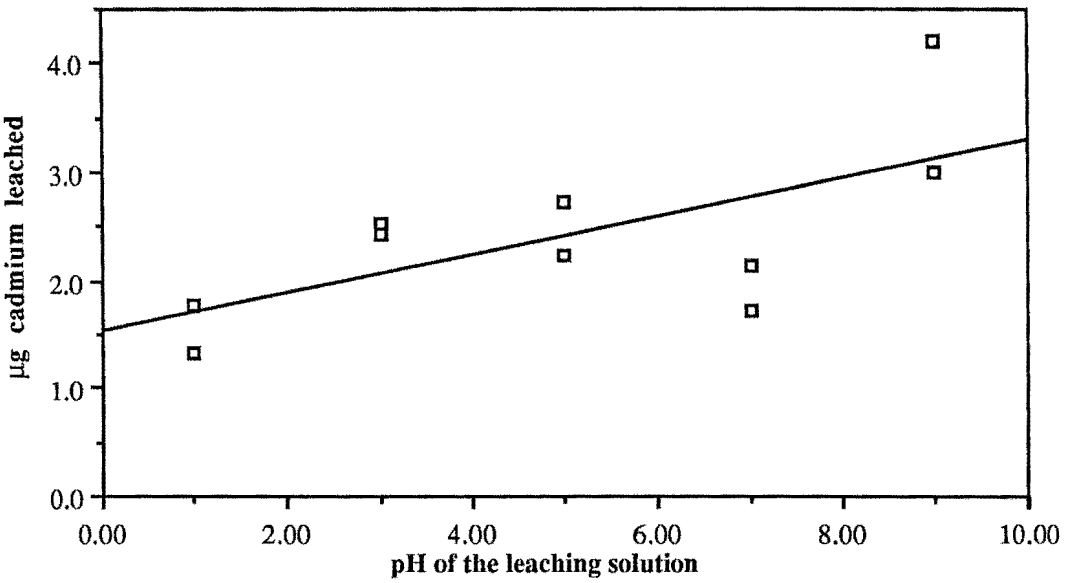


Table 13·2

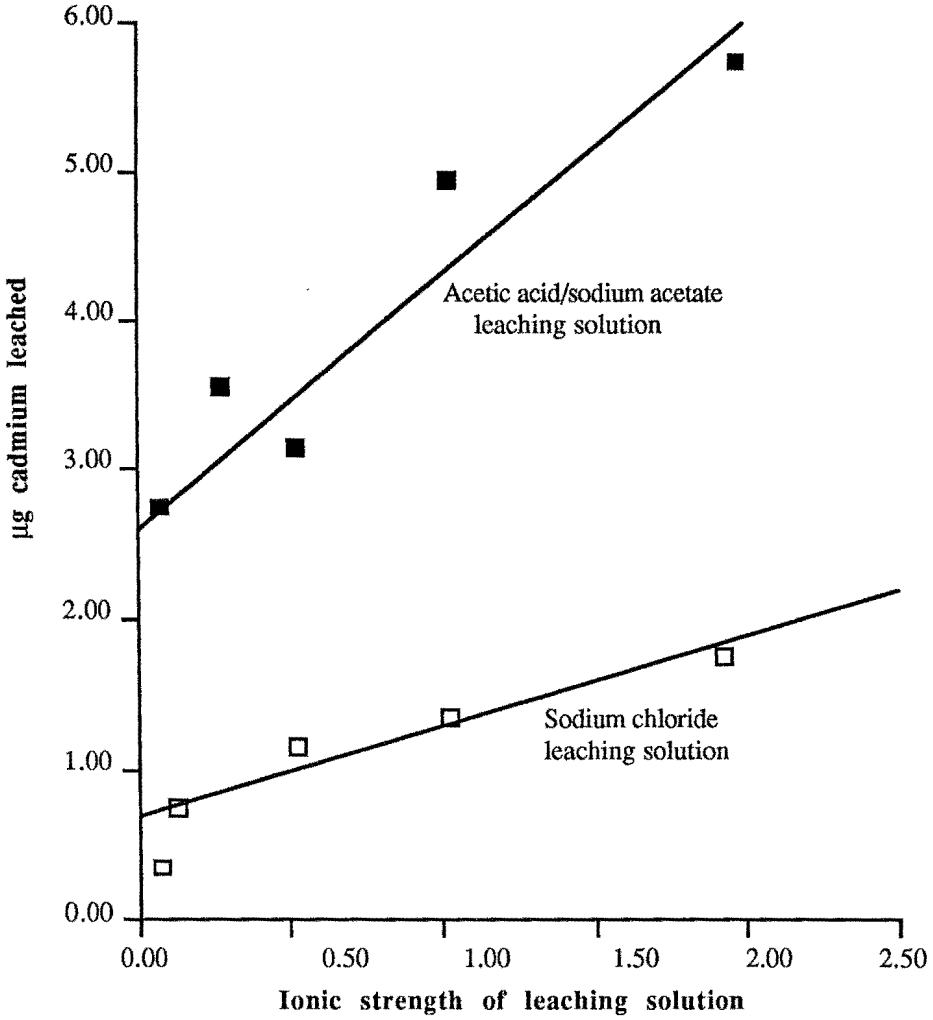
Correlation coefficients, probabilities and equations of the relationships between the amount of cadmium leached from the cadmium-containing paint and (a) the pH and ionic strength of the acetic acid/sodium acetate leaching solution, and (b) the ionic strength of the sodium chloride solution.

Relationship between μgCd leached and...	Correlation coefficient	Probability	Significance	Least-squares relationship[a]
pH of acetic acid/sodium acetate leaching solution	0.656	<0.05	Just	μgCd leached = 0.18pH + 1.52
Ionic strength of acetic acid/ sodium acetate solution	0.836	<0.01	Very	μgCd leached = 1.71I + 2.61
Ionic strength of sodium chloride leaching solution	0.912	<0.05	Just	μgCd leached = 0.61I + 0.69

Note: **a.** Where I is the ionic strength.

Figure 13·3

Relationships between the amount of cadmium lost from the cadmium-containing paint and the ionic strength and type of anion in the leaching solution at pH 5. (In the case of the acetic acid/sodium acetate leaching solution, each plotted point is the mean of two determinations.)



Surprisingly, increasing the acidity of the leaching solutions did not cause more cadmium to be released from the cadmium-containing paint—in fact, it had the opposite effect (Figure 13·2). A "just significant" positive linear relationship exists between the pH of the acetic acid/sodium acetate leaching solutions and the amount of cadmium leached from the paint (Table 13·2).

The results of these experiments cannot be directly compared with the results of experiments relating to the adsorption of cadmium by soils at various acidities given in Chapter 10, for two reasons: firstly, the chemical forms of cadmium in the soil were likely to have been different from those in the paint; and secondly, liberation of cadmium in the weathering experiments may well have proceeded under kinetic (rather than thermodynamic) control, due to the short residence time of the leaching solution droplets.

From the discussion in section 5·3·2 it would seem likely that the species of cadmium in the paint was a cadmium thioselenide ($CdS_xSe_{(1-x)}$); cadmium atoms on the paint's surface were therefore likely to have been chemically bound to sulphur and selenium atoms.

Liberation of cadmium from the paint's surface could have come about by one or all of the following mechanisms:

1. Competition by sodium ions and hydrogen ions (in the leaching solutions) for sites occupied by cadmium.
2. Complexation of cadmium by acetate ions and the formation of (highly soluble) cadmium acetate ($Cd(C_2H_3O_2)_2$) (Weast and Astle, 1983).
3. Attack and solubilization of sulphur and selenium atoms by complexation with sodium ions and hydrogen ions (to form such compounds as NaHS, NaHSe, Na_2S and Na_2Se), with concomitant release of cadmium by mechanical dislodgement (Weast and Astle, 1983).

Of the range of acetic acid/sodium acetate leaching solutions used to study the effect of acidity (all of which were of ionic strength 0.1), those of higher pH would have had proportionately more sodium ions and proportionately less hydrogen ions than those of lower pH; however, all of the solutions would have had the same concentration of acetate anions. It is likely, therefore, that the pH effect observed was a result of changing the ratio of sodium ions to hydrogen ions, and that under the conditions of the experiment, sodium ions were more efficient than hydrogen ions in causing the ultimate liberation of cadmium from the paint. (Unfortunately, because of the probable role of sodium ions in the leaching process, nothing definite can be said about the effect of pH *alone* on the amount of cadmium leached from the paint.)

Increasing the ionic strength of the acetic acid/sodium acetate leaching solutions caused more cadmium to be released from the cadmium-containing paint (Figure 13·3 and Table 13·2), an effect which could be attributed to an increased importance of the mechanisms for cadmium release outlined above (1–3) with higher concentrations of sodium ions, hydrogen ions and acetate anions in the leaching solutions.

A similar ionic strength effect was observed when using sodium chloride solutions as the leaching reagents (Figure 13·3 and Table 13·2). Cadmium's ability to form soluble chloride complexes ($CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, $CdCl_4^{2-}$ and $CdCl_6^{4-}$) at chloride ion concentrations of greater than 0.001 M is well documented (Eichenberger and Chen, 1982; Hahne and Kroontje, 1973; Weber and Posselt, 1976). Formation of such complexes could in this case be substituted for the second mechanism for cadmium release listed above.

The slope of the relationship between the amount of cadmium lost from the paint and the ionic strength of the sodium chloride solutions is 2.8 times less than that observed in the case of the acetic acid/sodium acetate leaching solutions, and overall, the latter solutions appeared to leach 3.6 times more cadmium than the former (Tables 13·1 and 13·2). As both types of leaching solutions used were (more or less) of the same pH, and as sodium was the cation in both cases, the differences observed could reflect differences in the intrinsic abilities of acetate anions and chloride ions to solubilize cadmium from the paint: *i.e.* chloride ions may be less efficient at solubilizing cadmium from the paint than acetate anions. Another possible explanation for the differences observed is that the Chelex 100 resin, used to isolate cadmium from the salt solutions, may have failed to chelate all of the cadmium if some of it

was in a chloride-complexed form. However, this seems unlikely, as Chelex 100 has been reported to be capable of efficiently removing trace metal ions from most naturally occurring ligands in seawater (Hahne and Kroontje, 1973; Kingston *et al.* 1978; Smith, 1974). Furthermore, the first stability constant of cadmium complexation by chloride ions is 2 240 times lower than that of cadmium complexation by iminodiacetic acid, a close derivative of which comprises the chelating groups of Chelex 100 resin (Bjerrum *et al.* 1957 and 1958; Högfeldt, 1982).

Thus, it seems likely that the differences between the amounts of cadmium detected in acetic acid/sodium acetate solution leachates and the amounts detected in the (processed) sodium chloride solution leachates are due to intrinsic differences in the abilities of acetate anions and chloride ions to solubilize cadmium. This effect could be related to the fact that chloride ions are monodentate ligands whereas acetate anions are bidentate in nature.

Overall, the weathering of cadmium from items coated with cadmium-thioselenide containing paints in the environment is likely to be influenced by sunlight, salinity, the concentrations and types of ligands which can form soluble complexes with cadmium in the rainwater, and the presence of cations in the rainwater.

13·3·2 Weathering of galvanized-iron

Results of the weathering experiments on the galvanized-iron sheet are given in Appendix 13·2, and the mean amounts of cadmium and zinc lost from the galvanized-iron sheet with each type of leaching solution are listed in Table 13·3.

Table 13·3

Mean amounts of cadmium and zinc lost from the galvanized-iron sheet with each type of leaching solution.

Leaching solution	Cadmium (μg)			Zinc (μg)		
	Mean	Std dev	95% error[a]	Mean	Std dev	95% error[a]
Double-deionised water (pH 4.10)	<0.01			84	19	±26
Rainwater (pH 4.32)	0.014	0	0	4 130	460	±2 900
0.1 M acetic acid/sodium acetate (various acidities)	<0.2			47 000	36 000	±32 400
pH 5.0 acetic acid/sodium acetate (various ionic st)	<0.6			94 000	18 400	±16 600

Note: a. Student's t-test error on mean.

Substantial amounts of zinc were leached from the galvanized-iron sheet under all of the conditions investigated, whereas cadmium was detected only in the preconcentrated rainwater leachates (Appendix 13·2 and Table 13·3). (Low levels of cadmium already

present in the acetic acid/sodium acetate leaching solutions made preconcentration pointless in these cases (section 13·2·3).)

Metallic zinc is thermodynamically unstable in water under a wide range of conditions (Posselt and Weber, 1976), and zinc detected in the leachates presumably represented metallic zinc (from the surface of the galvanized-iron) which had been oxidised (to Zn^{2+}) during the course of the experiments. Release of cadmium may have proceeded by two processes (a) direct oxidation of metallic cadmium, and (b) mechanical dislodgement and solubilization of cadmium (at the atomic level) during the corrosion of zinc (Posselt and Weber, 1976). Because zinc is oxidised more readily than cadmium ($E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V; $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V), it would be expected that direct oxidation of cadmium within the zinc surface of the galvanized-iron would be inhibited by zinc offering cathodic protection (Posselt and Weber, 1976).

The mean concentrations of zinc and cadmium in the original galvanized-iron (three samples of which were analysed) were (54 000 ± 5 400) μgZn g^{-1} and (0.225 ± 0.039) μgCd g^{-1} (section 4·3·2)—the mean zinc/cadmium ratio in the galvanized-iron was therefore 240 000. This can be compared with the mean ratio of zinc/cadmium in the rainwater which had been passed over the galvanized-iron sheet, which was 295 000 (Table 13·3). The similarity of the two ratios suggests that loss of cadmium from the surface of the galvanized-iron was primarily governed by the loss of zinc (under the experimental conditions used). Weber and Posselt (1976), who examined cadmium corrosion under conditions designed to approximate those found in water distribution systems, also reported that the rate of cadmium loss from a galvanized-iron surface was determined by the rate of zinc loss.

It can be calculated from the data in Table 13·3 that a volume of (the same) rainwater equivalent to Christchurch's average annual rainfall might be expected to leach 9 μg of cadmium and 2.63 g of zinc from a sheet of galvanized-iron of area 1 m^2 (assuming that the supply of leachable cadmium and zinc did not become exhausted). Thus, the weathering of (unpainted) galvanized-iron products may make a major contribution to environmental zinc levels in Christchurch (due both to the leaching characteristics of the galvanized-iron and the prevalence of galvanized-iron products in Christchurch). This result is in agreement with the correlation between rainfall and dissolved zinc concentrations in Christchurch riverwater, discussed in section 9·3·2. Assuming that the zinc/cadmium ratios in most galvanized-iron products in the environment are similar to or higher than that in the galvanized-iron sheet investigated in this study (an assumption which is not necessarily correct) it would be expected that the contribution made by weathering of galvanized-iron products to environmental cadmium levels would be comparatively small.

Double-deionised water leached about 50 times less zinc from the galvanized-iron than equal volumes of rainwater, a difference which is possibly due to the former leaching solutions possessing lower ionic strengths than the latter (Table 13·3).

Relationships between the amount of zinc leached from the galvanized-iron and the pH and ionic strength of the acetic acid/sodium acetate leaching solutions are illustrated in Figures 13·4 and 13·5. Although cadmium could not be detected in leachates from these

experiments, it would seem likely that the amount of zinc released would determine a "lower limit" to the amount of cadmium liberated.

Figure 13·4

Effect of acidity of the 0.1 M acetic acid/sodium acetate leaching solutions on the amount of zinc lost from the galvanized-iron sheet.

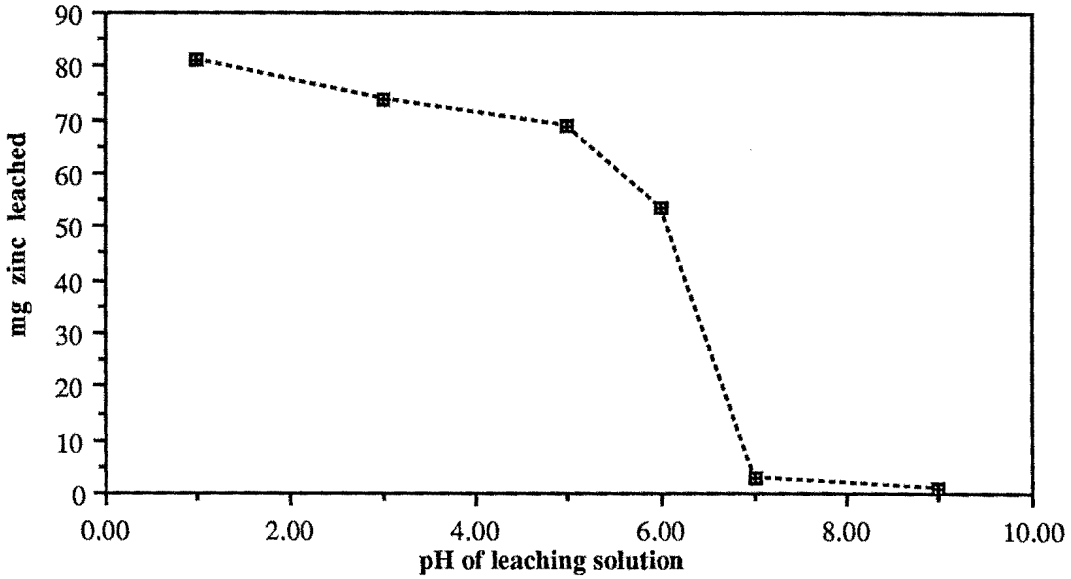
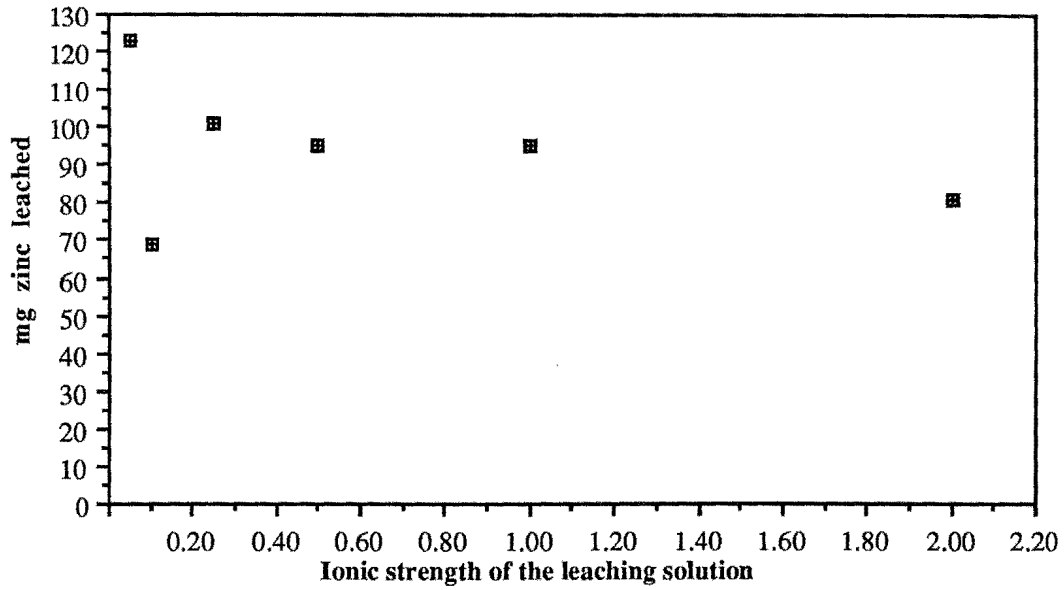


Figure 13·5

Effect the ionic strength of the acetic acid/sodium acetate leaching solutions on the amount of zinc lost from the galvanized-iron sheet. (All leaching solutions were of pH 5.0.)



Comparatively little zinc was lost from the galvanized-iron using acetic acid/sodium acetate leaching solutions of pH 9.00 and 7.00. However, further decreasing the pH from 7.00 to 6.00 caused a sharp (seventeenfold) increase in the amount of zinc liberated (Figure 13·4 and Appendix 13·2). This increase probably represents the large-scale stabilization of

simple ionic zinc (Zn^{2+}) at pH 6.00, a species which is reported to be thermodynamically stable below pH 7 (Hermann and Neumann-Mahlkau, 1985). Decreasing the pH of the leaching solutions to 5.00, 3.00 and 1.00 caused small (but steady) increases in the amount of zinc lost from the galvanized-iron.

The implication of these results in terms of the environment is that significantly more zinc (and therefore cadmium) is likely to be weathered from galvanized-iron products when the pH of the rainfall drops below 6–7.

At pH 5.00 (and over the range of ionic strengths studied: 0.05–2.00) the amount of zinc lost from the galvanized-iron sheet was independent of the ionic strength of the acetic acid/sodium acetate leaching solutions ($R = 0.347$, $p > 0.1$) (Figure 13·5 and Appendix 13·2). However, acetic acid/sodium acetate solutions (at pH 5.0) were on average 23 times more efficient than rainwater (pH 4.32) and 1 120 times more efficient than double-deionised water (pH 4.10) at leaching zinc from the galvanized-iron (Table 13·3). These differences could be due to acetate anions in the acetic acid/sodium acetate solutions facilitating in the removal of zinc by formation of zinc acetate (Weast and Astle, 1986). It is also possible that the rate of zinc loss from galvanized-iron may be sensitive to ionic strength effects only under conditions where the ionic strength of the leaching solution is less than 0.05.

13·4 Conclusion

The weathering of products coated with the cadmium-containing paint is likely to cause the release of a certain amount of cadmium to the environment, as even the most "mild" leaching solutions used (double-deionised water) gained detectable levels of cadmium from the paint. Mean amounts of cadmium leached per 1 000 ml of leaching solution ranged from 0.41 μg (using double-deionised water before UV irradiation) to 11.3 μg (using rainwater after UV irradiation)—implying that a square metre of the paint could lose somewhere between 260–7 180 $\mu gCd\ year^{-1}$ assuming that the supply of leachable cadmium was not exhausted in the process (an assumption which is not necessarily correct).

The amounts of cadmium lost from the paint were increased by raising the ionic strength of the leaching solutions and by exposure of the paint to ultra-violet radiation. The type of anion in the leaching solutions also appeared to influence the amount of cadmium lost from the paint, with acetate anions leaching about three times more cadmium from the paint than chloride ions. (It was not possible to determine the effect of acidity.) It seems probable that in the environment, factors such as sunlight, salinity, the concentrations and types of ligands which can form soluble complexes with cadmium in the rainwater, and the concentrations of cations in the rainwater would all be likely to influence the amount of cadmium weathered from the cadmium-containing paint.

Substantial amounts of zinc were leached from the galvanized-iron sheet under all of the conditions investigated, whereas losses of cadmium were comparatively small (or below detection limits). Assuming that the supply of leachable cadmium and zinc on the surface of the galvanized-iron did not become exhausted, a volume of rainwater equivalent to

Christchurch's average annual rainfall might be expected to leach 9 μg of cadmium and 2.63 g of zinc from a sheet of galvanized-iron of area 1 m^2. Weathering of unpainted galvanized-iron products is could (therefore) be an important source of environmental zinc and a minor source of environmental cadmium in Christchurch (given the prevalence of galvanized-iron products in Christchurch).

The mean ratio of zinc/cadmium in the rainwater which had been passed over the galvanized iron was 295 000, and that of the galvanized iron itself was 240 000. The similarity of these two ratios suggests that loss of cadmium from the galvanized-iron sheet was governed by the loss of zinc.

Decreasing the pH of the leaching solutions from 7.00 to 6.00 caused a sharp (seventeenfold) increase in the amount of zinc lost from the galvanized-iron sheet, suggesting that substantially more zinc (and therefore cadmium) is likely to be weathered from galvanized-iron products when the pH of the rainfall drops below 6–7. The amount of zinc lost from the galvanized-iron sheet was independent of the ionic strength of the acetic acid/sodium acetate leaching solutions over the ionic strength range 0.05–2.00.

13·5 References

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13·6 Appendices

Appendix 13·1 (section 13·3·1)

Results of weathering experiments relating to the cadmium-containing paint. (All leaching solutions were of 1 000 ml volume, and experiments are listed in the order in which they were conducted.)

Leaching solution	µg cadmium leached from the painted surface
Double-deionised water (pH 4.10)	
Run 1	0.44
Run 2	0.44
Run 3	0.34
0.1 M acetic acid/sodium acetate	
Run 1	
pH 9.0	4.20
pH 7.0	2.13
pH 5.0	2.23
pH 3.0	2.33
pH 1.0	1.33
Run 2	
pH 9.0	3.00
pH 7.0	1.72
pH 5.0	2.72
pH 3.0	2.53
pH 1.0	1.78
Mean of the two runs (Student's t 95% error in brackets)	
pH 9.0	3.70 (±4.48)
pH 7.0	1.93 (±1.83)
pH 5.0	2.48 (±2.21)
pH 3.0	2.43 (±0.88)
pH 1.0	1.56 (±2.02)
pH 5.0 acetic acid/sodium acetate	
Run 1	
Ionic strength: 0.10	2.23
0.25	3.55
0.50	3.15
1.00	5.05
2.00	4.40
Run 2	
Ionic strength: 0.10	2.72
0.50	3.10
1.00	4.88
2.00	7.15

Appendix 13·1 continued...

Leaching solution		µg cadmium leached from the painted surface
Mean of the two runs (Student's t 95% error in brackets)		
Ionic strength:	0.10	2.48 (±2.21)
	0.25	3.55
	0.50	3.13 (±0.13)
	1.00	4.97 (±0.76)
	2.00	5.78 (±12.28)
Sodium chloride solution		
Ionic strength:	0.05	0.40
	0.10	0.82
	0.50	1.22
	1.00	1.44
	2.00	1.78
Experiments after the UV irradiation		
Double-deionised water		
	Run 1	2.69
	Run 2	2.63
	Run 3	1.99
	Run 4	2.36
	Run 5	2.59
	Run 6	2.59
	Run 7	2.79
	Run 8	2.39
	Run 9	2.22
	Run 10	2.49
Rainwater (pH 4.50)		
	Run 1	12.1
	Run 2	10.5

Appendix 13·2 (section 13·3·2)

Results of weathering experiments relating to the galvanized-iron surface. (All leaching solutions were of 1 000 ml volume, and experiments are listed in the order in which they were conducted.)

Leaching solution		µgZn leached	µgCd leached
Double-deionised water (pH 4.10)			
	Run 1	94	<0.01
	Run 2	105	<0.01
	Run 3	65	<0.01
	Run 4	71	<0.01
Rainwater (pH 4.32)			
	Run 1	3 800	0.014
	Run 2	4 450	0.014

Appendix 13·2 continued...

Leaching solution	µgZn leached	µgCd leached
0.1 M acetic acid /sodium acetate		
pH 9.0	1 070	<0.2
pH 7.0	3 140	<0.2
pH 6.0	53 500	<0.2
pH 5.0	69 000	<0.2
pH 3.0	74 000	<0.2
pH 1.0	81 000	<0.2
pH 5.0 acetic acid/sodium acetate		
Ionic strength: 0.05	123 000	<0.2
0.10	69 000	<0.2
0.25	101 000	<0.2
0.50	95 000	<0.4
1.00	95 000	<0.8
2.00	81 000	<1.5

CHAPTER 14
EXPERIMENTAL METHODS

14·1 Introduction

In this chapter, the various experimental methods which were used in this thesis are described in further detail. Aspects relating to the preparation and handling of samples and standards are discussed in section 14·2, and descriptions of the instrumental techniques and parameters used are found in section 14·3.

14·2 Aspects of the preparation and handling of samples

Contamination of samples, by either the analyte or other materials which alter the analytical response, can be a serious problem in the analysis of trace metals (Mattingley, 1988; Sharma *et al.* 1982; Wilson, 1974). Potential sources of contamination include the apparatus and reagents used, the analyst, and the laboratory air (Dabeka and Ihnat, 1987). Throughout this study, the following precautions were taken in order to minimize contamination:

1. All reagents used were of high purity, having been either initially obtained in a highly pure form (AR grade or better), or obtained in a less pure form and distilled or recrystallised before use. Dilution of samples, standards and blanks was achieved using double-distilled (or double-deionised Milli-Q) water. Stock solutions of 1 000 $\mu g\ ml^{-1}$ cadmium, copper, lead, selenium and zinc (from which the working standards were eventually derived) were prepared by dissolution of the appropriate amounts of AR cadmium sulphate ($3CdSO_4.8H_2O$), copper sulphate ($CuSO_4.5H_2O$), lead nitrate ($Pb(NO_3)_2$), selenium (Se) and zinc sulphate ($ZnSO_4.6H_2O$), respectively, in 1 000 ml (each) of 0.1 M nitric acid. Diluted samples of these stock solutions were checked by FAAS against other stock solutions of cadmium, copper, lead, selenium and zinc which were already in existence.
2. Prior to being used for the first time, all glassware and plastic apparatus was washed with soapy water, soaked in 4 M AR nitric acid for at least 48 hours, washed thoroughly with double-distilled water and dried. Between uses, equipment was rinsed with tap water, soaked in 4 M AR nitric acid for a minimum of 16 hours, rinsed thoroughly with double-distilled water and dried. The purpose of the acid-washing was to leach and/or desorb any contaminants from surfaces which would come into contact with samples or standards (Kinsella and Willix, 1982). Red and yellow plastic volumetric-flask tops were found to contain significant quantities of cadmium (section 5·3·1), and were thus discarded in favour of polypropylene and glass volumetric-flask tops.

4. Disposable plastic ("Med-X") gloves were worn when handling most samples, to reduce the risk of contamination from the analyst.
5. The number of steps in each analytical method used were kept to a minimum, as the risk of samples becoming significantly contaminated generally increases as the method becomes more complex (Wilson, 1974).
6. When appropriate (and possible), samples likely to contain low concentrations of cadmium were handled in a (class 100) Clean Room, in order to minimize contamination from fallout of airborne particulates. In the normal laboratory, the length of time that samples were exposed to the laboratory air was minimized (for example, a watch-glass was placed over each sample being digested). Concentrations of cadmium, lead and zinc in the air of the Clean Room and concentrations of cadmium, copper, lead and zinc in the air of two frequently used "normal" laboratories were measured using the methods outlined in section 7·2, and are listed in Table 14·1.

Table 14·1

Mean concentrations of cadmium, lead and zinc in the air of the Clean Room and cadmium, copper, lead and zinc in the air of two "normal" laboratories often used during this study.

	Cadmium	Copper	Lead	Zinc
Clean Room				
Number of samples	5		5	5
Mean concn (ng m^{-3})	<0.21		<0.5	1.6
Standard devn (ng m^{-3})				0.7
95% error[a] (ng m^{-3})				±0.7
The two laboratories				
Number of samples[b]	15	6	15	15
Mean concn (ng m^{-3})	0.98	3.03	134	40.8
Standard devn (ng m^{-3})	0.69	2.82	64	24.1
95% error[a] (ng m^{-3})	±0.33	±2.54	±30	±11.3

Notes: a. Student's t-test error on mean.
b. One outlier was removed.

Comparison of the data listed in Table 14·1 with that given in Table 7·2 reveals that the mean concentrations of cadmium, copper, lead and zinc in the air of the two laboratories are similar to mean levels of the four metals in external Christchurch air, and (as such) are fairly low. Cadmium, lead and zinc concentrations in the air of the Clean Room were substantially lower than concentrations of the three metals in the air of the two laboratories (Table 14·1).

Only one definite source of cadmium contamination was identified during the course of this research: substantial amounts of cadmium were leached from the red and yellow painted markings on a new batch of glass pipettes when they were acid-washed, causing contamination of one batch of samples, standards and blanks. It seems likely that these

markings had been made with paints containing cadmium sulphide (yellow) and cadmium thioselenide (red) (section 5·3·2). (Unpainted pipettes were used before and after this event.)

Some types of yellow plastic disposable pipette tips have previously been found to contain significant quantities of cadmium (Pruszkowska *et al.* 1983). Ten translucent yellow-tinted disposable pipette tips—of a type commonly used during this thesis—were boiled for 30 minutes in 15 ml of AR 4 M nitric acid. No cadmium was detected by GFAAS in the resulting solution (detection limit: 0.15 $\mu g\ l^{-1}$), implying that the particular variety of pipette tips used in this study were not likely to have contained cadmium (section 5·3·3).

All liquid samples were analysed as soon as possible after being prepared, in order to minimize potential losses of analytes which could occur by adsorption to the container walls (Chen and Zhang, 1984).

14·3 Instrumental techniques and parameters

14·3·1 Atomic Absorption Spectrometry

Most analyses performed in this study were carried out using Flame Atomic Absorption Spectrometry (FAAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The former analyses were carried out on a Varian AA-1475 Atomic Absorption Spectrophotometer, and the latter on a GBC 903 Single Beam Atomic Absorption Spectrophotometer coupled to a (GBC) GF 1000 Controller Unit.

In both FAAS and GFAAS, radiation is produced which corresponds in wavelength to a given resonance transition of the element of interest. (A *resonance transition* is one of equivalent energy to the energy gap between an atom's ground state and one of its excited states.) Ground state atoms of the target element (produced in either the flame or the graphite furnace) absorb a portion of the resonance radiation, whereas other atoms do not. The intensity of the resonance radiation which has passed through the sample is thus proportional to the concentration of atoms capable of absorbing that radiation (Kenner and Busch, 1979).

In this study, hollow cathode lamps were used to produce the required wavelengths of radiation; the type of metal being analysed (or an alloy of it) comprised the cathodes of these lamps. Applying a voltage to each lamp causes excitation of the atoms in the cathode, and decay of each excited atom back to the ground state is accompanied by the emission of a quantized packet of resonance radiation (Price, 1974).

The primary difference between GFAAS and FAAS is the means of sample atomization employed. In FAAS, the liquid solution is converted into a fine mist (by passage through a nebulizer) which is then passed into a flame. Energy from the flame causes evaporation of the solvent and dissociation of a portion of the compounds in the sample, forming (among other things) a population of ground state atoms. Using FAAS, only a small fraction of the total amount of atoms aspirated eventually contribute to the analytical signal, as the efficiency of the nebulization process is low and the residence time of atoms in the flame is short (Culver, 1975; Price, 1974).

In GFAAS, a small volume of the liquid sample (2 µl in this study) is injected into a cylindrical graphite tube (the *graphite furnace*), which is then heated by electrical resistance. Because the sample is stationary and atomization occurs suddenly, a higher density of ground state atoms are produced for a longer time period using the graphite furnace method of atomization than when using a flame, the overall effect of which is that the sensitivity of GFAAS is substantially (20–500 times) higher than that of FAAS for most elements (Culver, 1975).

In the GFAAS analyses in this study, the graphite furnace heating cycles consisted of four temperature steps. Steps 1 and 2 were designed to cause the steady, even and complete evaporation of solvent from the sample (and are termed drying steps), and step 3—the "ashing" step—was designed to thermally decompose (and remove) as much of the sample matrix as possible (especially organic material) without removing the analyte. The purpose of step 4, which comprised a rapid increase in the temperature, was to decompose analyte molecular species in order to form a population of ground state atoms (Culver, 1975).

Both FAAS and GFAAS are subject to various chemical and physical interferences, all of which influence the proportion of atoms available to absorb resonance radiation. Physical interferences in both techniques, their causes, and the means by which they were counteracted in this study were as follows:

1. Emission of resonance radiation during the decay of excited atoms in the flame or furnace: this is caused by the flame or furnace being too hot. To overcome this problem, the radiation from the hollow cathode lamp is pulsed, allowing a distinction between the radiation attributable to both sources and that caused by decay of excited sample atoms only (Price, 1974). The overall signal is adjusted accordingly (automatically).
2. Scatter and background absorption of the resonance radiation. Scatter of the resonance radiation is caused by the presence of small solid particles in the resonance beam, and the presence of molecular species which are capable of absorbing the particular wavelength of resonance radiation used causes "background absorption" (molecular species are often capable of absorbing radiation over a wide range of wavelengths). Scatter tends to increase the amount of analytical noise, and both scatter and background absorption increase the overall absorption signal (Kenner and Busch, 1979; Price, 1974; Pruszkowska *et al.* 1983). The extra analytical noise caused by scatter can be reduced by avoiding samples with high concentrations of dissolved solids, or by dilution of the samples (Kenner and Busch, 1979). In all analyses performed in this study, the extra absorbance caused by scatter and background absorption were automatically adjusted by comparison of the attenuation of the resonance signal with that of a (broad spectrum) deuterium lamp. A higher atomization temperature (causing dissociation of molecular species) can also be used to reduce background absorption.
3. Variations in the physical properties of the sample solutions. The viscosity and surface tension of sample solutions influences the efficiency of sample nebulization (and thus atomization) in the case of FAAS and the heating characteristics of the sample in the

graphite furnace in the case of GFAAS. Errors can thus occur if the physical properties of the standard solutions used to construct a calibration curve are dissimilar to those of the sample solutions (Kenner and Busch, 1979; Price, 1974). Throughout this study, care was taken to ensure that the physical composition (such as acidity) of the standard solutions and the sample solutions were as similar as possible.

Two types of chemical interference can occur in the flame during an analysis by FAAS: (a) a proportion of the target element may react with other substances to form stable compounds, and (b) a fraction of the the target element may ionize in the flame. Both of these processes decrease the concentration of free ground state atoms available in the flame to absorb resonance radiation, and become a problem if the chemical composition of the calibration standards differs significantly from that of the unknown sample (Kabil and Mostafa, 1985; Kenner and Busch, 1979). Significant ionization does not occur in GFAAS because of the high electron densities associated with the electrical method of heating the graphite furnace (Powell, 1986); however, stable compounds are known to form in the graphite furnace (Mubarak *et al.* 1978).

Two precautions were taken in this study in order to minimize the effects of chemical interferences. Firstly, complex sample matrices were generally simplified during preparation for analysis by FAAS or GFAAS. Foods and tree leaves, for example, were ashed to remove organic matter prior to being digested (sections 6·2 and 8·2·2). Secondly (and as mentioned above) calibration standards were given similar chemical compositions to those of samples.

Chemical interferences can be detected by comparison of the slope of the normal calibration curve with the slope of a curve derived from the analysis of samples to which standards have been added (Culver, 1975; Price, 1974). In almost all cases, this method failed to detect the presence of significant chemical interferences (as would be shown by a difference in the slopes of the two curves of greater than 5%), implying that the precautions taken to protect against chemical interferences were in most cases sufficient. One strong chemical interference did occur in the GFAAS analysis of cadmium in the presence of high concentrations of magnesium ions; this interference was eliminated by matrix modification of the samples using phosphoric acid (as has already been described in section 12·2·3).

Parameters relating to all FAAS analyses of cadmium, copper, lead, selenium and and zinc which were carried out during the course of this thesis are listed in Table 14·2.

Graphite furnace heating programs used in all GFAAS analyses of copper, lead and zinc are given in Table 14.3; those used in the analysis of cadmium have been given in preceding chapters. Other parameters relating to the GFAAS analyses of cadmium, copper, lead and zinc undertaken in this study are listed in Table 14·4. The graphite furnace heating programs were initially optimised in order to obtain the strongest atomic absorption signals.

Table 14·2

Parameters relating to the FAAS analyses of cadmium, copper, lead, selenium and zinc.

	Cadmium	Copper	Lead	Selenium	Zinc
Lamp current (mV)	4	4	5	8	5
Wavelength (nm)	228.8	324.8	217.0	196.0	213.9
Slit width (nm)	0.5	0.5	1.0	1.0	1.0
Deuterium background correction facility	On	On	On	On	On
Flame					
Fuel	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene
Oxidant	Air	Air	Air	Air	Air
Oxidant:fuel ratio	5	5	5	5	5

Table 14·3

Furnace heating programs used in the GFAAS analyses of copper, lead and zinc.

Metal	Step No.	Step	Temp (°C)	Ramp time (seconds)	Holding time (seconds)
Copper					
	1	Drying # 1	80	4	4
	2	Drying # 2	120	3	3
	3	Ashing	400	4	1
	4	Atomization	2 500	1	2
Lead					
	1	Drying # 1	80	5	5
	2	Drying # 2	120	5	5
	3	Ashing	300	4	1
	4	Atomization	2 200	1	2
Zinc					
	1	Drying # 1	80	5	5
	2	Drying # 2	120	5	5
	3	Ashing	340	4	1
	4	Atomization	2 100	1	2

Table 14·4

Other parameters relating to the GFAAS analyses of cadmium, copper, lead, and zinc.

	Cadmium	Copper	Lead	Zinc
Lamp current (mV)	4	4	5	5
Wavelength (nm)	228.8	324.8	217.0	213.9
Slit width (nm)	0.6	0.5	1.0	1.0
Deuterium background correction facility	On	On	On	On
Size of sample (µl)	2.0	2.0	2.0	2.0
Inert gas[a]	OFN	OFN	OFN	OFN

Note: **a**. OFN = oxygen-free nitrogen.

The temperature values in the graphite furnace heating programs listed in Table 14·3 and in the preceding chapters are those which were programmed into the particular machine used—however, some evidence was obtained (using an optical pyrometer) that the actual temperatures achieved in the graphite furnace were slightly lower than programmed temperatures in the atomization step (Powell, 1988). For example, programmed temperatures of 2 000 °C and 2 500 °C were likely to have resulted in actual graphite furnace temperatures of about 1 800 °C and 2 250 °C, respectively.

14·3·2 X-ray Powder Diffractometry

Use of the technique of X-ray powder diffraction (XRPD) for the (qualitative) identification of various crystalline species was mentioned in Chapters 3, 5, 10 and 12.

In XRPD, a finely powdered crystalline sample is irradiated with a monochromatic beam of X-rays of known wavelength, and angles and intensities of X-rays which are diffracted by the crystals are measured. Spacings between parallel sets of lattice planes ("d-spacings") are then calculated according to the Bragg equation:

$$n\lambda = 2d \sin \theta$$

where λ is the wavelength of the X-rays, θ is the diffraction angle of the X-rays, n is the order of the diffraction, and d is the d-spacing. The set of d-spacings (and intensities) obtained is a function of the characteristics of the unit cell of the crystal, and as such is unique to each type of crystal (Kenner and Busch, 1979). (As the crystals in the sample are randomly oriented, information about spatial relationships between the different sets of lattice planes of a given crystal is not obtained by XRPD.)

All XRPD analyses in this work were carried out using a Phillips PW 1729 X-ray generator and a scintillation counter; these were coupled to a computer (which was used both

for the collection of data, and calculations). Samples were irradiated with copper radiation of wavelengths 1.54060 Å, 1.54444 Å and 1.53438 Å, which was produced by electron bombardment of a copper block (at 50 kV and 35 mA). Other details of the XRPD analyses undertaken in this study have been given in section 3·2·1 and section 5·2.

14·3·3 Anodic Stripping Voltammetry

Use of Anodic Stripping Voltammetry (ASV) was mentioned in sections 9·2·3 and 9·3·3. In ASV, a hanging mercury drop (which comprises the bottom end of a mercury electrode) is placed in the solution to be analysed. (The concentration of electrolytes in this solution must be sufficient to easily facilitate the electrochemical reactions, and the analyte must be a metal which forms an amalgam with mercury.) Two steps are then taken:

1. The electrodeposition step: the solution is stirred and an electric potential more negative than the reduction potential of the analyte is applied to the mercury electrode, causing cations of the analyte in solution migrate to the mercury drop and there be reduced. The amount of preconcentration achieved during this step is dependent on the electrodeposition time used.
2. The stripping step: the stirrer is turned off and (after the solution has become quiescent) the electric potential of the mercury electrode is scanned toward more positive values; Oxidation of the analyte in the mercury drop occurs when the potential of the mercury electrode matches the analyte's reduction potential, and is detected as an increase in electric current. The size of the current increase is proportional to the concentration of analyte in solution (Bard and Faulkner, 1980).

In this study, a new mercury drop was dispensed for each determination. Oxygen-free nitrogen was bubbled through each 20 ml sample solution for several minutes prior to the electrodeposition step, in order to remove oxygen from the system. During analyses, oxygen-free nitrogen was passed over the surface of each solution.

Other parameters used in the ASV analyses carried out in this study have been listed in Table 9·3.

14·3·4 Electron microprobe analysis

Use of electron microprobe analysis was mentioned in Chapter 3. In this technique, the solid sample is bombarded with a narrow beam of high-energy electrons (typically 25 kV). Atoms on the surface of the sample absorb the energy of some of the electrons, and then release it again in the form of X-rays, which are analysed for wavelength and intensity by an X-ray spectrometer. The X-rays' wavelengths are characteristic of the emitting element, and their intensities are proportional to the concentration of that element on the surface of the sample (Bain *et al.* 1986; Hill and Sawney, 1971). The technique allows qualitative and quantitative analysis of sample surface areas as small as 1 μm^2 (providing that the concentrations of the elements being analysed are sufficiently high); an example of its use is in the mapping of the distribution of macroelements in undisturbed soils (Dawson *et al.* 1985; Qureshi *et al.* 1978).

Other comments concerning the use of electron microprobe analysis in this study are found in sections 3·2·1 and 3·3·3b.

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CHAPTER 15
CONCLUSION

15·1 Introduction

The objectives of this study were to gather and interpret information relating to (a) the concentrations of cadmium in the environment, and (b) the chemistry of cadmium in the environment. Detailed conclusions to the experimental work carried out in these two areas have been given in Chapters 3–13. General conclusions relating to cadmium (only) will be reviewed in this chapter.

15·2 Concentrations of cadmium in the environment

A summary of the means, confidence intervals and ranges of the cadmium concentrations found in the various substances examined during the course of this thesis is given in Table 15·1.

Table 15·1

Means, confidence intervals and ranges of cadmium concentrations in the various materials examined during this study.

Material	Cadmium concentration				Section reference
	Mean	95% error[a]	Range	Geometric or weighted mean[b]	
Soil ($\mu gCd\ g^{-1}$)					
Background	0.104	±0.098	0.068–0.158		3·3·2a
Residential[c]	0.326	±0.074	0.114–0.789		3·3·2a
Industrial	0.375	±0.073	0.169–0.880		3·3·2b
Road-dust ($\mu gCd\ g^{-1}$)					
Residential	0.774	±0.269	0.463–1.58		3·3·2a
Industrial[c]	7.39	±4.12	0.339–200		3·3·2b
House-dust ($\mu gCd\ g^{-1}$)	5.15	±0.63	0.557–21.0	4.24	4·3·1
Air $ngCd\ m^{-3}$	0.694	±0.191	0.043–6.29	0.411	7·3·1
$\mu gCd\ g^{-1}$	36.7	±7.2	1.45–235	21.0	& 7·6
Riverwater ($\mu gCd\ l^{-1}$)	0.16	±0.05	0.06–0.51	0.14	9·3·1
Horse-chestnut leaves ($\mu gCd\ g^{-1}$ ash)	0.197	±0.034	0.085–0.489	0.177	8·3·1
Foods ($\mu gCd\ kg^{-1}$)	20.4	±10.4	0.02–179	8.84	6·3·1
Commercial products[d] ($\mu gCd\ g^{-1}$)	5 580	±7 110	0.072–235 000		5·3·1

Notes: **a.** 95% confidence error on mean: Student's t-test for $n<30$ and Normal distribution for $n\geq30$.
b. If calculated or applicable. **c.** Excluding sequentially extracted samples (section 12·3·2).
d. Excluding values below the detection limit.

Although high levels of cadmium were often found in road-dust from the immediate vicinity of industrial operations involving cadmium, concentrations of cadmium in the wider Christchurch environment (such as the air, riverwater and soil) were generally low. Interestingly, Christchurch house-dusts contained higher concentrations of cadmium than typical external dusts (Chapter 4). Cadmium concentrations in some commercial products were very high; however, there appeared to be little risk of cadmium being significantly mobilized during the use of most of these products (Chapter 5).

Ingestion and inhalation are the principal means by which cadmium enters the human body (section 1·4·2). Estimates of the contributions made by air, food and water, road dust and house dust to daily cadmium absorption in Christchurch adults and children are presented in Table 15·2 (these were derived from the data given in Chapters 3,4, 6, and 7).

Table 15·2

Estimates of the contributions of food and water, air, road-dust and house-dust to the amount of cadmium absorbed by Christchurch adults[a] and young children.

	Mean Cd concn	Daily intake[b]	Daily Cd intake (μg)	μg Cd absorbed per day[c]	% of total μg Cd absorbed per day
Adults					
Food & water	8.84 μg kg^{-1}[d]	2.5 kg	22.1	1.326	99.7–99.8
Air	0.411 ng m^{-3}[e]	22 m^3	0.009	0.002–0.004	0.2–0.3
House-dust	4.24 μg g^{-1}[e]	0 g	0	0	0
Road-dust	4.08 μg g^{-1}[f]	0 g	0	0	0
Total				1.328–1.330	
Young children					
Food & water	8.84 μg kg^{-1}[d]	1.20 kg	10.608	2.652	96.2–99.6
Air	0.411 ng m^{-3}[e]	7 m^3	0.003	0.001	<0.1
House-dust	4.24 μg g^{-1}[e]	0.005–0.05 g	0.021–0.212	0.005–0.053	0.2–2.0
Road-dust	4.08 μg g^{-1}[f]	0.005–0.05 g	0.020–0.204	0.005–0.051	0.2–1.9
Total				2.663–2.757	

Notes: **a.** Assuming they are not occupationally exposed to cadmium, are non-smokers and do not consume significant quantities of oysters.
b. Sources: Duggan and Williams, 1977; Fergusson, 1990; Muskett *et al.* 1979; Snyder *et al.* 1975.
c. Assuming that 6% and 25% of ingested Cd is absorbed by adults and children, respectively, and that 25–50% of inhaled Cd is absorbed by both adults and children (Fergusson, 1990; Förstner, 1980).
d. Mean weighted according to consumption of the various food groups.
e. Geometric mean.
f. Mean of industrial and residential means.

The average amount of cadmium absorbed each day by a non-occupationally exposed, non-smoking, non-oyster-eating Christchurch adult is likely to be about 1.33 μg, of which, food and water are likely to account for over 99% (Table 15·2). It is probable that absorption of cadmium by (these) adults through the inhalation of air is negligible when compared with cadmium absorption from dietary sources (0.2–0.3%). The estimated dietary intake of cadmium by Christchurch adults (22.1 $\mu g\ day^{-1}$) is 3–4 times below the maximum tolerable dietary cadmium intake recommended by the World Health Organization (section 6·3·2).

Similarly, food is likely to account for most (96.2–99.6%) of the cadmium absorbed by young children in Christchurch, and the total amount of cadmium absorbed through inhalation and the ingestion of house-dust or road-dust is likely to be negligible when compared with the amount normally absorbed by young children from food sources (Table 15·2 and sections 3·3·2b and 4·3·1).

Overall, it would seem highly unlikely that present environmental levels of cadmium in Christchurch would constitute a chronic health risk to members of the non-occupationally exposed population who are non-smokers and who do not consume significant quantities of oysters.

Factors which influence (or may influence) the levels of cadmium in the various materials examined are numerous, and are discussed more fully in the *results and discussion* and *conclusion* sections of the preceding chapters.

15·3 Chemistry of cadmium in the environment

Studies relating to the chemistry of cadmium, and the main findings from these studies, were as follows:

1. Speciations of cadmium in industrial dust samples (section 3·3·3): cadmium concentrations in industrial dust samples generally increased with decreasing particle size, but showed no fixed relationship to particle density or magnetism.
2. Speciations and leaching behaviour of cadmium in yellow and red plastics (section 5·3·2): some yellow plastics contained cadmium sulphide (CdS), and some red plastics contained cadmium thioselenide (commonly as $CdS_{0.6}Se_{0.4}$). Small amounts of cadmium were leached from these plastics under "simulated stomach conditions".
3. Speciations of cadmium in Christchurch riverwater (section 9·3·3): about 40% of the cadmium in samples of Avon River water was soluble in n-octanol, and would be expected to be capable of crossing a biomembrane with relative ease. "Labile", "organically bound" and "inorganically bound" cadmium (as detected by ASV) comprised 70%, 20% and 10% of the total cadmium in the <0.025 μm fraction of (other samples of) Avon River water.
4. Behaviour of cadmium in a Christchurch soil (Chapters 10 and 11): A Christchurch soil showed a marked ability to adsorb trace quantities of cadmium (Chapter 10), and the mobility of cadmium in this soil was low (Chapter 11), findings which suggested

that cadmium applied to Christchurch soil is likely to accumulate surface layers rather than leach to the ground-water. Isotherms for cadmium adsorption by the soil and its components were generally linear. Amounts of cadmium adsorbed by the various fractions of the soil under identical conditions followed the order clay > whole soil > soil without iron and manganese oxides > silt > sand > soil without organic material > silica sand. The amount of cadmium adsorbed by the soil could be decreased by raising the acidity (which also had the effect of increasing cadmium's mobility) and by addition of competing (lead and zinc) ions to the system. Mobility of cadmium through the soil at pH 3.00 was found to be highly dependent on the form of cadmium deposited on the soil surface.

5. Behaviour of cadmium in samples undergoing sequential extraction, and the speciations of cadmium in environmental samples as determined by sequential extraction: Reagent selectivity for various forms of cadmium during application of a particular sequential extraction scheme was in some cases good and in some cases poor; however, little true redistribution of cadmium between phases occurred during the course of each sequential extraction. An alternative classification scheme for the forms of cadmium determined by this sequential extraction method was proposed. Most (80–90%) of the cadmium in residential soil, industrial road-dust and house-dust samples was likely to have been adsorbed, and/or carbonate bound, and/or strongly bound to easily reducible manganese oxides and amorphous iron oxides.
6. Weathering of cadmium from a surface finished with a cadmium-containing paint and from galvanized-iron: the amount of cadmium leached from the surface of a cadmium-containing paint was increased by raising the ionic strength of the leaching solutions and by exposure of the paint to ultra-violet radiation. The type of anion also had an effect, with acetate anions leaching more cadmium from the paint than chloride ions. Comparatively small (or undetectable) amounts of cadmium and large amounts of zinc were leached from a sheet of galvanized-iron (under all conditions investigated). The zinc/cadmium ratio in rainwater leachates suggested that the loss of cadmium from the galvanized-iron sheet was governed by the loss of zinc. The acidity of the leaching solutions markedly effected the amount of zinc (and thus cadmium) lost from the galvanized-iron sheet.

Overall, it could be expected that entry of cadmium into the environment by weathering processes and the mobility of cadmium in Christchurch soils or dusts would generally be increased under conditions characterized by higher acidities, higher concentrations of competing cations, and higher concentrations of ligands which can form soluble complexes with cadmium. Cadmium in Christchurch soils and dusts can be mobilized with relative ease, suggesting that fairly subtle changes in environmental conditions may significantly alter cadmium's behaviour in these materials.

15·4 Recommendation

Due to the importance of foods as a source of cadmium, it is felt that future research into cadmium would be profitably spent monitoring—and/or finding means of maintaining acceptable levels of—cadmium in New Zealand foods.

15·5 References

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